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DEWAXING OF MINERAL OIL BY LIQUID–LIQUID EXTRACTION.*

By T. G. HUNTER† and T. F. BROWN.‡

SUMMARY.

The possibility of replacing the present low-temperature methods of dewaxing mineral oil by liquid–liquid counter-current extraction with a solvent at operating temperatures above the melting point of the wax but below the critical solution temperature of the wax and solvent has been examined.

Computations for the counter-current extraction of pure component systems of various liquid hydrocarbons and cetane using aniline as the solvent are first employed, and indicate that the best separations are obtained from naphthenic and paraffinic oils, but the number of theoretical stages required is high.

A triangular diagram, employing the physical property of V.G.C. to represent composition of waxy oil and with the solvent treated as if it were a third component, has been employed for phase-equilibrium representation of an oil–wax–solvent system. It has been shown that the tie-lines on such a diagram can be interpolated by a Bachman plot, while the wax content of solvent-free extract and raffinate phases can be obtained from a correlation between V.G.C. and wax content. Counter-current computations made on such a diagram obtained when using acetone at 25° C suggest that the separation brought about by this solvent is not particularly promisi ng.

Experimental continuous counter-current extraction on a laboratory scale employing aniline as a solvent suggests that, while the process can be worked, yields under the conditions employed with this solvent are lower than in the conventional low-temperature dewaxing methods. The results obtained confirm the conclusions arrived at from the computations made on the oil–wax–acetone diagram that the separation achieved using a 15 per cent wax-stock charge is not as economic as the present commercial methods. There are indications from the computations made on pure components that wax stocks of higher wax content can be treated much more efficiently.

INTRODUCTION.

THE present low-temperature methods of dewaxing mineral oil are not entirely satisfactory. The chilling of an oil or an oil-solvent mixture, the maintenance of low temperature during subsequent handling and filtering or centrifuging of an oil or oil-solvent mixture, is in the aggregate an expensive process. In addition, the filtering or centrifuging step is a most laborious operation, being generally unsatisfactory, and aggravated by the necessity of maintaining low temperatures.

In systems consisting of oil, paraffin wax, and solvent at temperatures above the melting point of the paraffin wax it should be possible to employ the principle of solvent extraction to separate the wax and oil. Such a process would consist of extracting the wax-containing oil with a suitable solvent or solvent mixture at an operating temperature equal to, or above,

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* Paper read at Joint Meeting of the American Institution of Chemical Engineers and the Institution of Chemical Engineers (British) in Detroit, November 1947.

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the melting point of the wax present in the wax-containing oil, but below the critical solution temperature of the wax and the solvent. In this process the extract obtained after the removal of solvent would constitute the dewaxed oil. The raffinate would consist either of an oil-wax mixture with a wax content higher than the wax content of the original oil or would consist of a wax fairly free from oil, depending upon the extraction conditions employed. The extraction process could be carried out by batch extraction or more efficiently by counter-current extraction. Such an extraction process should be a simple one, easily operated and entirely free from expensive and troublesome chilling, filtering, and centrifuging operations. Compared with conventional low-temperature methods, it would appear to have practical and economic advantages.[14]

Separation of wax and oil by solvent extraction at temperatures above the melting point of the wax is theoretically possible. With a system consisting of a wax, oil, and solvent in which each of these materials is a single, pure component, the two definite types of equilibrium diagram illustrated

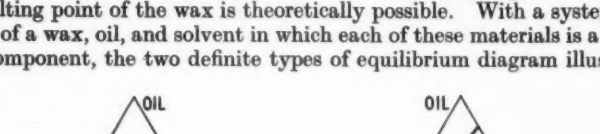

FIG. 1.

COMPARISON OF SINGLE AND DOUBLE NON-CONSOLUTE TERNARY PHASE DIAGRAMS.

in Fig. 1 can be obtained. Fig. 1 (*a*) represents the equilibrium data for such a system where the wax and solvent are two non-consolute liquids, while Fig. 1 (*b*) represents a similar system where both the wax and solvent and the oil and solvent are non-consolute liquid pairs.

In the single non-consolute pair system pure oil completely free from wax can never be obtained by solvent extraction, although theoretically pure wax free from oil can be produced. Dewaxed oil with the lowest wax content which can be reached is that represented by point x in Fig. 1 (*a*). In the case of the double non-consolute system, however, both pure oil and pure wax can be obtained, and complete or nearly complete separation of the oil and wax is theoretically possible.

Several references to the use of such a process are to be found in the literature. In 1920 the Deutsche Erdöl A.G. patented a process [5] for separating solid and liquid hydrocarbons. This consisted of liquefying the mixture to be separated by heating, and extracting, the liquefied mixture in counter-current with a solvent in which the solid hydrocarbons were practically insoluble, but in which the oily hydrocarbons were soluble. Diggs and Page [6] have claimed a process in which wax and oil were separated by treating the wax and oil with solvent at a temperature above the melting

point of the oil-wax mixture and subsequently cooling to separate the bulk of the wax as a liquid layer. Dearborn and Gee [4] have claimed the selective-solvent extraction of an oil with furfural at high temperature, whereby the paraffin wax is concentrated in the raffinate phase, in the liquid state, followed by dewaxing this phase, using the acetone–benzol process at low temperatures in the usual way. A. B. Brown [3] has patented the counter-current extraction of waxy petroleum oils at temperatures above the wax melting point with solvents such as cresylic acid. He carried out his extraction in a packed tower, and in the tower base the extract solution was cooled to release dissolved paraffins. Dewaxing by both batch and counter-current liquid extraction have also been proposed by A.-B. Separator-Nobel.[1] Katz [15] has published an account of the separation of oil and wax in the liquid phase at temperatures above the melting point of the wax by solvent extraction with cresol, while still later, in 1941, Hunter and Nash [9] patented a process for the separation of oil and wax by counter-current extraction in the liquid phase at a temperature above the melting point of the wax.

The present paper describes an investigation into the possibility of separating oil and wax, particularly low-melting-point waxes, by extraction with a solvent at temperatures above the melting point of the wax whereby the process is performed as a liquid–liquid extraction operation. The first part of the investigation is confined to counter-current extraction studies on pure component systems, similar in type to those of Fig. 1, where one component of the binary mixture to be separated is a solid at normal room temperatures.

Computations on Pure Component Systems.

In the pure component systems studied, cetane was selected to represent the solid component, and at the chosen temperature of equilibrium (25° C) cetane, melting point 18° C, is in the liquid state and therefore fulfils the requirements of the contemplated operation. The liquid hydrocarbons used in this work were *normal*-heptane, *cyclo*hexane, and benzene.

Aniline was chosen as a solvent principally in view of the fact that an initial investigation of the aniline points of several waxy-oil fractions indicated the possibility of separating wax and oil from these in the liquid phase by the use of this solvent. In addition, a preliminary determination of the individual solubilities of the various selected hydrocarbons in this solvent showed that practical ternary equilibrium diagrams could be obtained at 25° C and would vary in type from single to double non-consolute pair systems.

Tie-lines and saturation curves were determined in the following ternary systems at atmospheric pressure and 25° C :—

(1) cetane–benzene–aniline;
(2) cetane–*cyclo*hexane–aniline;
(3) cetane–heptane–aniline.

The above data for these systems have already been reported in a previous publication [12] and show the first to be of the single non-consolute-pair type with the remaining two to be of the double non-consolute-pair class.

A constant stock mixture for treating and containing 30 per cent cetane together with a constant raffinate of 95 per cent cetane was assumed in each case, and the yield of solid cake (in this process the cetane raffinate) and dewaxed liquid (extract), composition of dewaxed liquid, and number of theoretical stages required were computed graphically from the ternary equilibrium diagrams representing the above three systems using the method of computation described by Hunter and Nash.[10] In order to compute the number of theoretical stages required to produce the desired raffinate from the given stock with a definite solvent–stock ratio it is necessary to be able to interpolate conjugation lines in the heterogeneous region of the equilibrium diagram. The method employed for this was that described in the International Critical Tables.[13]

Table I summarizes the results of these counter-current computations on the three selected pure component systems. On the comparison basis of the production of a constant-composition raffinate for a constant-stock mixture treated the solvent–stock ratio, number of theoretical stages, yield of dewaxed liquid, and composition of dewaxed liquid are listed in Table I.

TABLE I.

Separation of Cetane and Other Hydrocarbons by Counter-current Extraction with Aniline.

Stock treated: 30 per cent cetane, 70 per cent liquid hydrocarbon.
Raffinate: 95 per cent cetane, 5 per cent other hydrocarbon.

Hydrocarbon other than cetane.	Solvent–stock ratio.	Number of theoretical stages.	Yield of dewaxed liquid as percentage of stock treated.	Composition of dewaxed liquid, per cent cetane.
Benzene	1·66	1·9	91·8	24·8
„	2·05	1·9	87·6	20·8
„	2·57	1·8	84·3	17·9
„	3·31	1·7	83·0	16·7
„	4·55	1·6	83·0	17·0
„	6·52	1·4	87·6	20·8
*cyclo*Hexane	4·55	9·4	73·7	6·8
„	4·77	6·1	74·0	7·2
„	6·00	4·1	77·9	11·6
„	10·10	2·3	86·7	20·0
Heptane	14·20	4·1	73·9	7·0
„	16·50	3·1	74·8	8·1
„	19·80	2·9	79·3	13·0
„	24·00	2·1	90·3	23·0

In Figs. 2, 3, and 4 the data given in Table I above have been plotted against solvent–stock ratio. It will be perceived from these figures that in the case of the single-pair non-consolute system the percentage of cetane in the dewaxed liquid decreases with increasing solvent–stock ratio to a definite minimum value, after which an increase in this ratio results in more cetane remaining in the dewaxed liquid. In the case of the double non-consolute-pair systems an increase in the solvent–stock ratio increases the percentage of cetane remaining in the dewaxed liquid. From the relative

position of curves 1, 2, and 3 in Fig. 2 it is obvious that a change in the liquid hydrocarbon from aromatic to naphthene to paraffin results in a progressive increase in the difficulty of extraction. In the case of System 3,

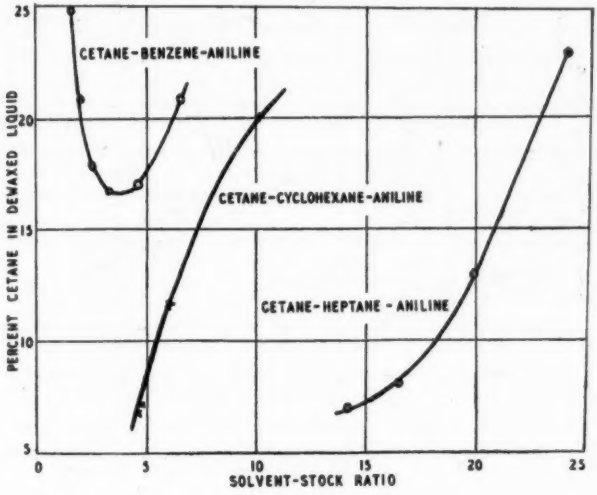

FIG. 2.

COMPUTATION OF QUALITY OF COUNTER-CURRENT PRODUCTS FROM BATCH EXPERIMENTS WITH PURE COMPONENTS.

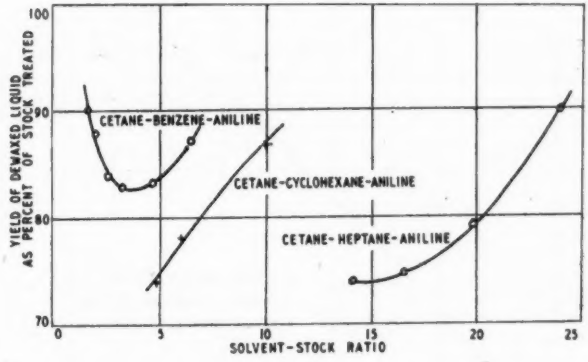

FIG. 3.

COMPUTATION OF YIELDS OF COUNTER-CURRENT PRODUCTS FROM BATCH EXPERIMENTS WITH PURE COMPONENTS.

where the second hydrocarbon is a pure paraffin, large solvent–stock ratios are required. The yield of dewaxed liquid produced, expressed as a percentage of the stock treated, decreases for the single non-consolute-pair system with increasing solvent–stock ratio to a minimum after which increasing

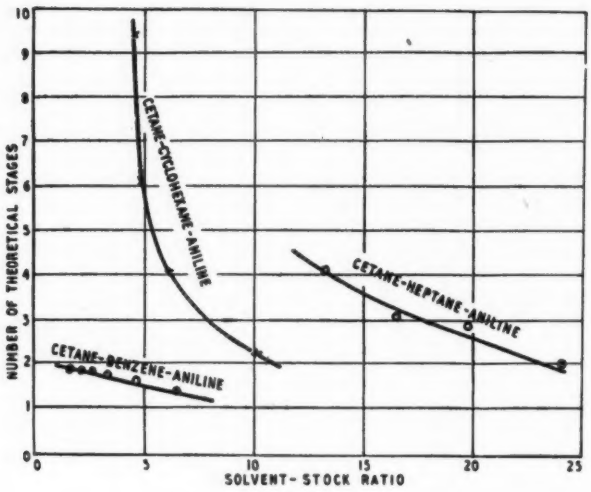

FIG. 4.

COMPUTATION OF NUMBER OF THEORETICAL COUNTER-CURRENT EXTRACTION STAGES USING BATCH DATA FROM PURE COMPONENT SYSTEMS.

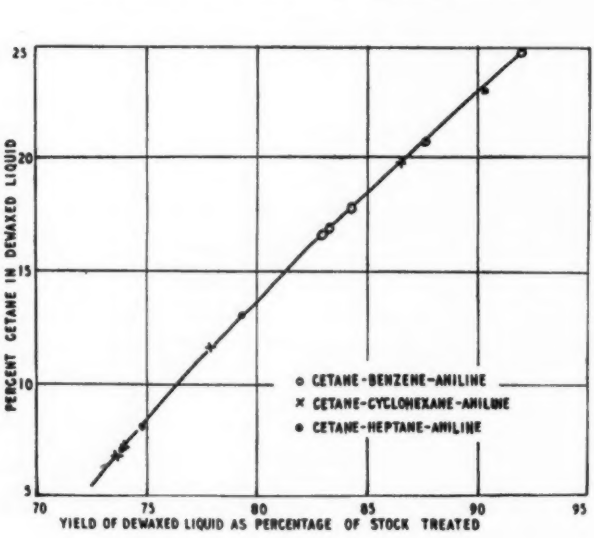

FIG. 5.

QUALITY–YIELD CURVE FOR THREE PURE COMPONENT SYSTEMS.

this ratio increases the yield of dewaxed liquid. For the other type of system investigated the yield of dewaxed liquid increases with increasing solvent–stock ratio. In Fig. 5 the yield of dewaxed liquid has been plotted against its composition as percentage cetane and, as one would expect, the yield is a simple function of the composition whereby the lowest yields are obtained with the highest degree of separation. It will be seen from Fig. 4 that for the single non-consolute-pair system, where the possible degree of separation is low, only a small number of theoretical stages are required. For the other type of system, where the possible extraction is greater, correspondingly more theoretical stages are necessary. As one would expect also, the number of theoretical stages required for a given separation increases as the liquid hydrocarbons change from aromatics through naphthenes to paraffins.

These computations indicate that it is possible to separate binary mixtures where one component of the mixture is a solid, by means of the proposed process. In a mineral-oil dewaxing process, however, the separation required is solid straight-chain hydrocarbons from a liquid hydrocarbon mixture of branched-chain and cyclic material. In the above results a change in the liquid hydrocarbons from cyclic to straight-chain resulted in a progressive increase in the difficulty of separation which was to be expected, so that the proposed process, when applied to oil–wax separations, may not be highly effective.

Similar computations were therefore applied to an oil–wax–solvent system, and for this purpose the phase-equilibrium diagram was first studied.

Oil–Wax–Solvent Equilibrium.

In the present work the choice of waxy oils for experimental work was very carefully made. In the first place natural refinery products were selected and synthetic mixtures avoided.

A sample of waxy oil was obtained which had been separated from a topped crude by vacuum distillation. This material, namely heavy oil and paraffin (hereinafter referred to as H.O.P.), is a waxy distillate with a boiling range of 95 per cent between 140° and 260° C under 20 mm pressure. The principle physical properties determined for this are shown in Table II.

Table II.

Physical Properties of H.O.P.

Density, $d_{60°}^{60°}$ F.	0·8788
Viscosity at 100° F, cs.	11·4
V.G.C.	0·8465
Refractive index, n_D^{20}	1·4894
,, ,, n_D^{20}	1·4851
Aniline point, ° C	80·1
Wax content, weight %	15·4

In solvent refining, Hunter and Nash [11] have used an additive physical property to represent composition of a lubricating oil on one side of a triangular graph with the solvent treated as if it were a third component. In this way they obtained a binodal curve for an oil–solvent system by treating an oil stock of fixed composition with varying proportions of solvent, and by applying data obtained from multi-stage and counter-current processes

they were able to show that this binodal curve could be used for multi-stage and counter-current extraction computations. Sage and Lacey [18] have also observed that complex natural mixtures exhibit behaviour comparable to that found for binary and ternary systems when such complex mixtures are considered from the standpoint of fixed composition.

The physical property used by Hunter and Nash was that of Viscosity Gravity Constant as developed by Hill and Coates [8] from a study of distillate fractions from a lubricating oil. This physical property was assumed to be additive over the commercial range of lubricating oils (*i.e.*, oils with V.G.C. between 0·78 and 0·87), and according to the work of Thompson [19] it is additive for the purposes of quantitative representation in solvent refining.

For the purpose of representing a wax-bearing mineral oil–solvent system in the present work it was decided therefore to employ the method of Hunter and Nash and several physical properties of oil–wax mixtures were investigated with a view to their use on a triangular diagram.

Choice of Solvent for Phase Diagrams.

As the equilibrium temperature chosen was 25° C (corresponding to that used for the pure components), aniline was found to be of little value, since the amount of oil dissolved was negligible at that temperature, and the properties of the extract were difficult to determine owing to its being so small in quantity.

Acetone was selected, since it gave a greater yield of each phase at 25° C, gave a better diagram, and besides being similar in its selective action to aniline, is at the moment an important refinery solvent in dewaxing processes of the chilling type.

Determination of Equilibrium Data.

A weighed quantity of filtered untreated oil stock was placed in a thermostatically controlled equilibrium vessel and agitated for 2 hr with a weighed quantity of filtered acetone previously dried over calcium chloride. The agitation was stopped and the two layers allowed to separate over a period of 5 to 6 hr.

Small, weighed, glass-stoppered funnels were used to sample the phases as they were run off. These samples were employed for the estimation of the acetone content.

The method used for acetone determination was Goodwin's [7] modification of the iodoform method of Messinger, and which is applicable to aqueous solutions containing 30 to 40 mg of acetone. The optimum conditions for the removal of solvent from acetone–oil mixtures were found to be distillation under moderate vacuum for 30 min, the final traces of acetone being removed by the passage of a stream of nitrogen through the oil for a further 30 min at 40° C.

Experimental Results.

Table III shows the results obtained for the system H.O.P.–acetone giving V.G.C., density, aniline point, and refractive index as the physical properties of the oil found in each phase. In some cases the experimental

data were found to give tie-lines which were, either by reason of incongruous slope or by reason of non-coincidence of the ends with the average saturation curve drawn through the others, rejected for representation purposes.

TABLE III.

Equilibrium Data H.O.P.–Acetone at 25° C.

Solvent/oil ratio.	Percentage acetone in		Refractive index at 30° C.		Aniline point.		Viscosity–gravity constant.	
	Extract.	Raffinate.	Extract.	Raffinate.	Extract.	Raffinate.	Extract.	Raffinate.
0·81	62·1	32·0	1·4964	1·4808	72·3	83·4	0·8688	0·8369
0·98	66·1	28·6	1·4970	1·4777	71·8	85·5	—	0·8338
1·26	69·2	27·0	1·4957	1·4758	72·6	87·6	0·8673	0·8302
1·33	69·8	26·1	1·4935	1·4750	72·1	88·2	0·8634	0·8287
1·49	71·3	25·6	1·4949	1·4743	73·1	89·2	0·8660	0·8274
1·66	72·6	24·1	1·4933	1·4725	73·8	90·0	0·8630	0·8240
1·98	74·3	22·7	1·4910	1·4716	74·5	90·3	0·8587	0·8223

In order to determine if the tie-lines and ternary diagram could be considered completely analogous to ternary systems of three pure components, an equation of the Bachman type was applied to the tie-lines curves. In a three-component system consisting of A, B, and C, Bachman [2] correlates tie-line data by a plot of x against x/y, where x is the percentage of A in the A-rich phase and y is the percentage of B in the B-rich phase, the resulting graph being a straight line.

For the purpose of the application of this type of equation to the tie-line

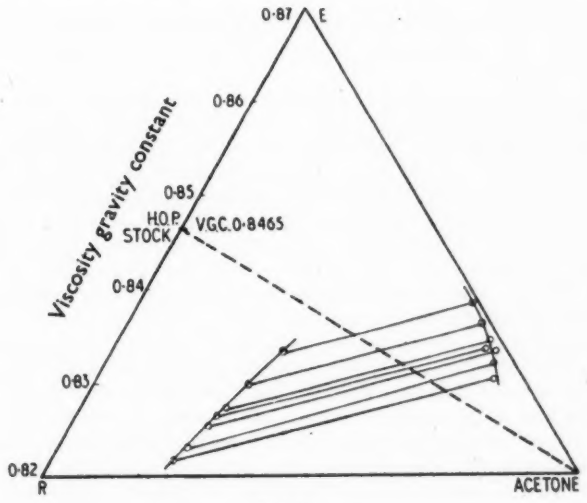

FIG. 6.

TERNARY PHASE DIAGRAM FOR HEAVY OIL AND PARAFFIN WITH ACETONE AT 25° C.

curves, ternary diagrams were constructed using V.G.C., density, refractive index, and aniline point as alternative physical properties of the oil, and all these diagrams were plotted on comparable scales. In order to make the Bachman correlation in the present case, the equilibrium diagrams were treated as if they were simple three-component equilibrium diagrams consisting of component E, component R, and solvent as shown in Fig. 6. The values chosen for plotting were :—

x = percentage of solvent in extract phase.
y = percentage of component R in raffinate phase.

It was found that the plot of x against x/y was a straight line only when the diagram was constructed in terms of V.G.C.

In order further to test the applicability of this result, all the previously used physical-property scales were doubled. Again, it was found that V.G.C. was the only property which gave an approximately linear graph.

It is therefore reasonable to conclude that in addition to providing a saturation curve which can fulfil the tests imposed on it from the standpoint of general applicability, the property of V.G.C. furnishes a ternary diagram the tie-lines of which can be interpolated by a Bachman plot. The equilibrium diagram for the system H.O.P.–acetone employing V.G.C. as the physical property is shown in Fig. 6.

Definition of Wax and Oil.

In addition to a careful choice of materials, a rigorous definition of wax and oil was made and adhered to. As a method of wax estimation was essential in the present work, the definition of wax was made to depend on this method.

The first step was to choose a suitable solvent which possessed the essential properties of a dewaxing solvent as outlined by Poole [17] and by Kalichevsky.[14]

As a dewaxing solvent for wax estimation, ethylene dichloride was tried, after the method of McKittrick,[16] and was found to be very successful for the particular oil used. Because the solubilities and intersolubilities of the wax, oil, and solvent in an intimate mixture vary at different temperatures and concentrations, no definite proportion of solvent to oil is generally applicable to all oils. In the present case, after several trial experiments, it was found that a ratio of 25 ml of ethylene dichloride to 1 g of oil–wax mixture maintained at — 35° C for a period of 1 hr with any precipitated material washed twice with 10 ml of chilled solvent was sufficient to give reproducible results.

The definitions of wax and oil are purely arbitrary and depend on the temperature of separation. When dealing especially with the lower-melting wax constituents of a given oil it becomes very obvious that there is no hard-and-fast line of demarcation between oils and waxes. In the present work an arbitrary conception of wax follows from the method outlined above for its estimation. Wax is therefore the white solid portion separated and filtered from the waxy oil by the addition of 25 ml ethylene dichloride per 1 g oil, chilling to — 35° C during a period of 1 hr, and washing twice with 10 ml chilled solvent.

The physical properties of the wax separated by this method from H.O.P. were as follows :—

Melting point 25° C
Refractive index 1·4305 at 60° C

Counter-current Extraction Computations on the H.O.P.–Acetone Diagram.

Several computations were made on the V.G.C. diagram for H.O.P.–acetone in order to compare the results obtained with those for pure components.

Table IV contains the results of these calculations which were made on a stock of V.G.C. 0·8465 (H.O.P.) containing 15·4 per cent wax and assuming a constant raffinate product of V.G.C. 0·8223. The percentage wax in the two solvent-free oil phases was obtained as follows :—

From the equilibrium experiments on H.O.P. a plot of V.G.C. *versus* percentage wax was made for both the solvent-free extract and raffinate phases. A smooth curve was obtained only in the case of the raffinate phase, the extract-phase plot giving a number of rather scattered points which appeared to pass through a maximum. The V.G.C. of the solvent-free raffinate phase as obtained by computation from the triangular diagram was therefore used together with the graph of V.G.C. *versus* percentage wax to obtain the percentage wax present in the solvent-free raffinate. By means of a weight balance the percentage wax present in the solvent-free extract was calculated.

Table IV.

Dewaxing of H.O.P. by Counter-current Extraction with Acetone.

Stock treated : H.O.P.; 15·4 per cent wax; V.G.C. 0·8465.
Constant raffinate : V.G.C. 0·8223; 21·2 per cent wax.

Solvent–stock ratio.	Number of theoretical stages.	Yield of dewaxed oil as percentage of stock treated.	Percentage wax in dewaxed oil.
0·92	2·19	52·6	10·2
0·99	1·91	52·0	10·0
1·14	1·64	53·2	10·3
1·52	1·25	56·9	11·0
1·84	1·00	62·5	11·9

In Fig. 7 the percentage of wax in the dewaxed oil, and the percentage yield of dewaxed oil are plotted against solvent–stock ratio. The curves obtained are similar in form to those in Figs. 2, 3, and 4 for the single-pair non-consolute system of pure components in which percentage of wax in the dewaxed liquid and the yield of the dewaxed liquid pass through a minimum. In the present case also the plot of percentage wax in dewaxed oil against yield of dewaxed oil is a simple straight-line function.

The dewaxing treatment in use at the refinery from which the H.O.P. was obtained during the period that the oil stocks were supplied was cold-pressing at — 18° C (0·3° F) to give " Once-cooled blue-oil " (1 C.B.O.). This

1 C.B.O. was further cold pressed at — 25° C (— 13·0° F) to give "Second-cooled blue-oil" (2 C.B.O.). The wax contents and approximate yields of these products from the cold-pressing operations are compared in Table V

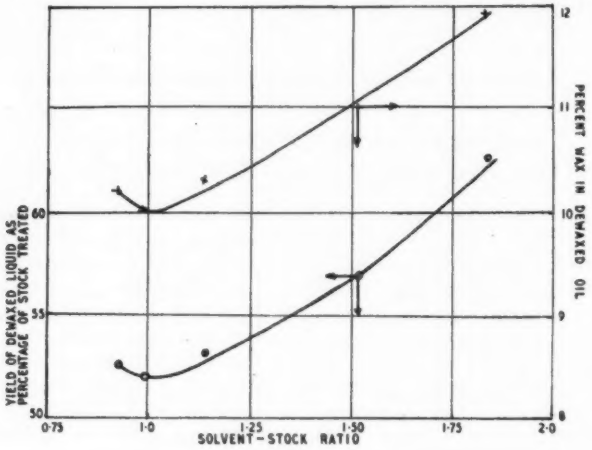

FIG. 7.

COMPUTATIONS OF YIELD AND QUALITY OF COUNTER-CURRENT PRODUCTS FROM BATCH DATA FOR H.O.P. AND ACETONE.

with those computed for the counter-current extraction of H.O.P. with acetone.

It will be seen from Table V that under the conditions employed the solvent-extraction method gives results comparable with the first cold-pressing

TABLE V.

Comparison of Cold Pressing and Dewaxing by Extraction.

Operation.	Operating temperature, ° C.	Solvent.	Solvent–stock ratio.	Yield of dewaxed oil, per cent of stock treated.	Wax content of dewaxed oil, %.
Liquid–liquid extraction . .	25	Acetone	0·9–1·8	52–63	10·0–11·9
Cold-pressing, 1st stage . . .	—18	None	—	80–85	10·6
Cold-pressing, 2nd stage . . .	—25	None	—	85–90	7·0
Cold-pressing, combined two stages .	—18 & —25	None	—	68–77	7·0

operation, but with the second cold-pressing a much lower wax content for the dewaxed oil results than any recorded in the extraction process. The yields from both cold-pressing operations are also greater.

Experimental Counter-current Extraction of H.O.P. with Aniline.

Experimental counter-current extraction was next tried out on H.O.P. on a laboratory scale using aniline as a solvent at operating temperatures above 50° C. Aniline was selected as a solvent because preliminary work showed that at these operating temperatures it gave promising extraction performance, a ready phase separation after mixing, and was easily separated from the oil by steam distillation.

Apparatus and Procedure.

The counter-current extraction apparatus employed consisted of an electrically heated 30-in × 1¼-in glass tower fitted with a vertical-paddle agitator, and supplied with oil and solvent by gravity feed through flow-meters and hot-water spiral pre-heaters. The column outlets led directly to storage vessels for extract and raffinate. The column and connexions were lagged throughout, and thermometers were situated at all inlets and outlets and also inside the column.

In an actual run the preheaters were regulated to the required operating temperature by adjusting the flow of hot water through them, and oil and solvent allowed to flow through the apparatus at fixed rates. When the column was about half full the heater and paddle were switched on and the paddle speed adjusted. The products leaving the column were allowed to run into the waste receivers during the first 2 to 3 hr operation while conditions were reaching a steady state. The extract and raffinate streams were then switched over to tared vessels and an observed run carried out. The flow-rates, as indicated, were used for calculating the prevailing solvent–stock ratios employed in the individual runs.

Treatment of Extracts and Raffinate.

Various methods of separating aniline from extracts and raffinates were investigated, and that found to be most satisfactory was steam distillation. An extract or raffinate was steam distilled until a clear distillate was obtained after which the distillation was continued for a further 15 min. The flask, containing the oil-and-water emulsion remaining from the steam distillation, was then immersed in an electrically heated glycerine bath maintained at 96° C until separation into two clear layers was obtained. The water layer was then separated from the oil which was dried over calcium chloride and finally filtered. The wax content of the dried oil was then determined by the modified McKittrick method described above.

Samples of extract and raffinate phases produced by the process were analysed for aniline content by the following method.

To 1 g of the oil–aniline mixture was added 0·5 ml of acetic anhydride; 50 ml of water were then added and the mixture allowed to stand at room temperature for about 50 min after which the hydrolysis was finally completed by heating for 10 min on a steam bath. After cooling the amount of acetic acid present was titrated with $N/5$ sodium hydroxide, using phenolphthalein as indicator. A blank experiment on 0·5 ml of acetic

anhydride was carried out at the same time, and the difference between the two titrations gave the amount of aniline present.

The presence of oil did not affect this estimation, and acetic anhydride was found to have no action on the particular oils used. The accuracy of the method is believed to be of the order $\pm$ 1·5 per cent.

Results.

A complete record of the test runs carried out with the equipment is shown in Table VI. At constant temperature the wax content of the dewaxed oil increases with increasing solvent–oil ratio. With approximately constant solvent–oil ratio and increasing temperature the wax content of the dewaxed oil also increases.

TABLE VI.

Experimental Counter-current Extraction of H.O.P. with Aniline.

Operating temperature, ° C.	Solvent–stock ratio.	Percentage aniline in		Dewaxed oil.		
		Raffinate phase.	Extract phase.	Yield as percentage of stock treated.	Percentage wax.	Aniline point, ° C.
59·5	1·92	17·6	57·1	62·7	6·8	53·0
68·7	2·17	27·0	70·4	62·8	9·7	63·4
69·9	2·00	20·5	81·8	41·7	8·8	58·8
70·3	3·25	53·5	96·4	16·6	10·5	65·0
79·7	1·90	37·1	75·9	54·5	11·9	71·8

Using aniline as solvent in the ratio of 2 : 1 solvent to oil the process should be operated for this particular charge stock at a temperature below 60° C to give a yield and wax content at all comparable with the overall yield and quantity from the two-stage low-temperature commercial process. Although a suitable wax content can be obtained, yields are not so high as in the present commercial process.

DISCUSSION.

The results show that a separation can be affected and that the basic principles of the method are sound. For successful yields and quality of product it is necessary to choose the most suitable solvent for the conditions employed and to utilize an extraction scheme with the correct number of theoretical stages. Since the above work was completed, several processes based on these principles have been adopted in the U.K. for the de-oiling of wax with extremely satisfactory results and have completely superseded the less economic "sweating" process.

ACKNOWLEDGMENT.

The authors' thanks are due to E. Thornton of the Anglo-Iranian Oil Company Ltd., who supplied the raw materials with which the practical work reported above was carried out in 1939.

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ON THE CHEMICAL COMPOSITION OF OXIDIZED MINERAL OILS.

By D. J. W. Kreulen (Fellow) and F. G. Kreulen van Selms.

Summary.

The chemical composition of an oxidized white oil and of an oxidized transformer oil has been investigated. The oxidation products which dissolve in both oils and also those which precipitate as "resins" from oxidized transformer oil are predominantly carbonyl-containing hydroxy acids and their anhydrides.

The molecular weights of all oxidation products, "resins" included, are about the same and equal that of fresh oil. The formation of larger molecules during oxidation was not observed. During fractionation of oxidized oils with the aid of solvents, different oxidation products, which show striking resemblance with respect to constitution, accumulate in one fraction or another according to the relative predominance of certain typical groups.

The ester value of oxidized oils points not to esters but to anhydrides.

The increase in viscosity of oxidized oils is not due to any increase in molecular weight but to the appearance of polar groups, among which carbonyl groups are the most effective.

Some results on the deterioration of a lubricating oil in an aircraft engine are reported.

For proper appreciation of this paper the statements made in a previous communication * should be reiterated :—

1. The oxidation velocity of white oils, *i.e.*, oils which do not contain aromatic rings, is not affected by the addition of glass powder.
2. The oxidation velocity of low-viscosity mineral oils which contain also aromatic rings is greatly influenced by the addition of glass powder.
3. During the oxidation of white oils peroxides are formed, but peroxide formation is not marked during oxidation of ordinary technical oils.
4. When strongly oxidized technical oils are stored, red-brown "resins" are precipitated. In the case of white oils this does not happen.

A white oil and a transformer oil of similar constitution (compare the ring analyses) being available, it was decided to analyse both as to oxidation products. The constants of these oils in their original condition are given in Table I.

The white oil was oxidized for its induction period at 105° C and then treated for 29 hr at 140° C. During this treatment its colour became yellow, but no "resin" was precipitated during subsequent storage. The oxidized white oil will be referred to as WO.

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* Kreulen, D. J. W., and Kreulen van Selms, F. G. "On the Influence of Glass on the Oxidation of Low-viscosity Mineral Oils", *J. Inst. Petrol.*, 1948, **34**, 930.

When a transformer oil is oxidized in the presence of glass, "resins" precipitate during subsequent storage. In a second successive oxidation at the same temperature but without glass, the oil darkens considerably in colour and more "resins" are precipitated. To obtain sufficient "resins" for analysis the transformer oil was first oxidized for 55 hr at 140° C in the presence of 750 sq. cm. of glass surface per 100 c.c. of oil. It was then oxidized for a further 20 hr at the same temperature without glass.

TABLE I.

Constants of Fresh Oils.

	White oil.	Transformer oil.
Molecular weight	420	330
Sp. gr. 20°/4°	0·8729	0·8644
Refractive index D/20	1·4771	1·4730
Viscosity at 20° C, cs	84	33
Ring analysis (wt.%) :		
Aromatic rings	0	2
Naphthenic rings	35	35
Paraffinic side chains	65	63
Average number of rings per mol	2·6	2·4

After some weeks a considerable amount of "resin" had precipitated. The "resin" was purified by precipitation from a benzene solution with a surplus of petroleum spirit. The oxidized "resin-free" oil is referred to as TO, and the oil-free "resins" as R. The oxidized transformer oil consisted of 3·4 per cent R and 96·6 per cent TO.

The scheme of treatment of oils WO and TO is set out in Fig. 1 * and of "resin" R in Fig. 2.

The analyses of the fractions obtained are given in Tables II, III, and IV.

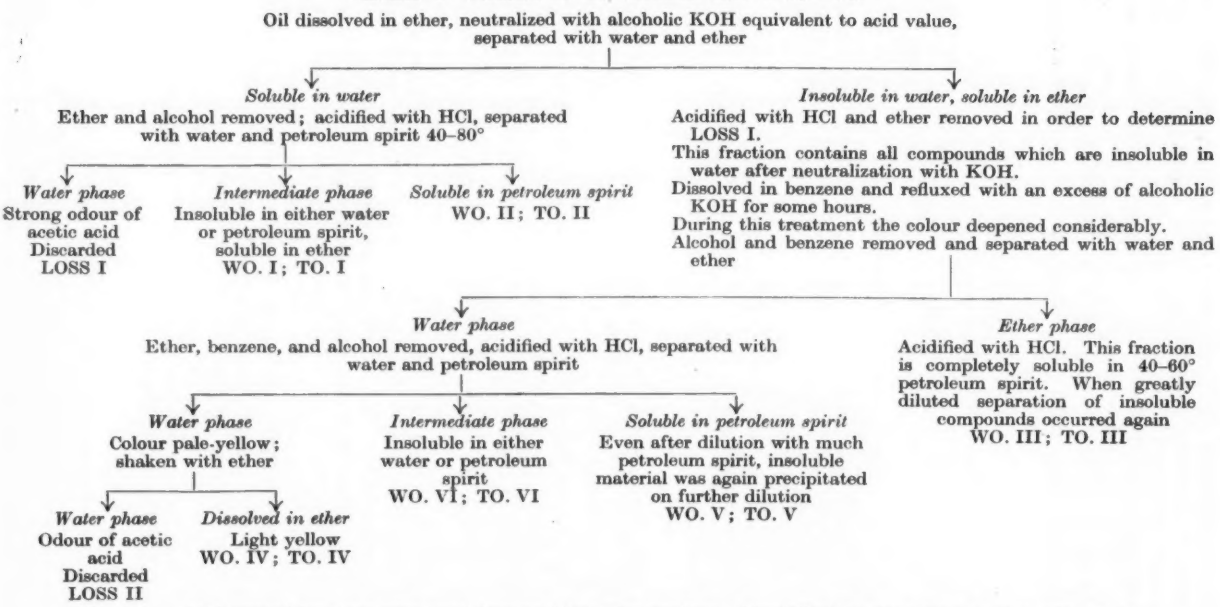
The values have been rounded off to the nearest tens as, on account of the small quantities of the substances available for the determinations, the accuracy is no greater. Also, the substances are not pure.

Molecular weights were determined cryoscopically using as solvents naphthalene, benzene, acetic acid, dioxane, or benzophenone. This was necessary as in some cases there was doubt as to whether or not the substance was completely dissolved. Complete solution, without any association, is essential. Consequently each molecular-weight determination was made with various solvents and the lowest figure reported. As an example of the effect of the solvent on molecular-weight determination it is stated that for the "resins" the figures were 1800 in benzene, 380 in dioxane, and 400 in benzophenone.

* During an attempt to separate volatile products from the oil by steam distillation, large quantities of white vapours with a pungent odour appeared in the condenser. The cause was found to be due to a loose joint allowing air to enter the condenser. The same phenomenon was observed during steam-distillation of the non-oxidized oil, showing that the steam-volatile compounds of low-viscosity oils are readily oxidizable.

FIG. 1.

METHOD OF WORKING UP THE OXIDIZED OILS TO AND WO.

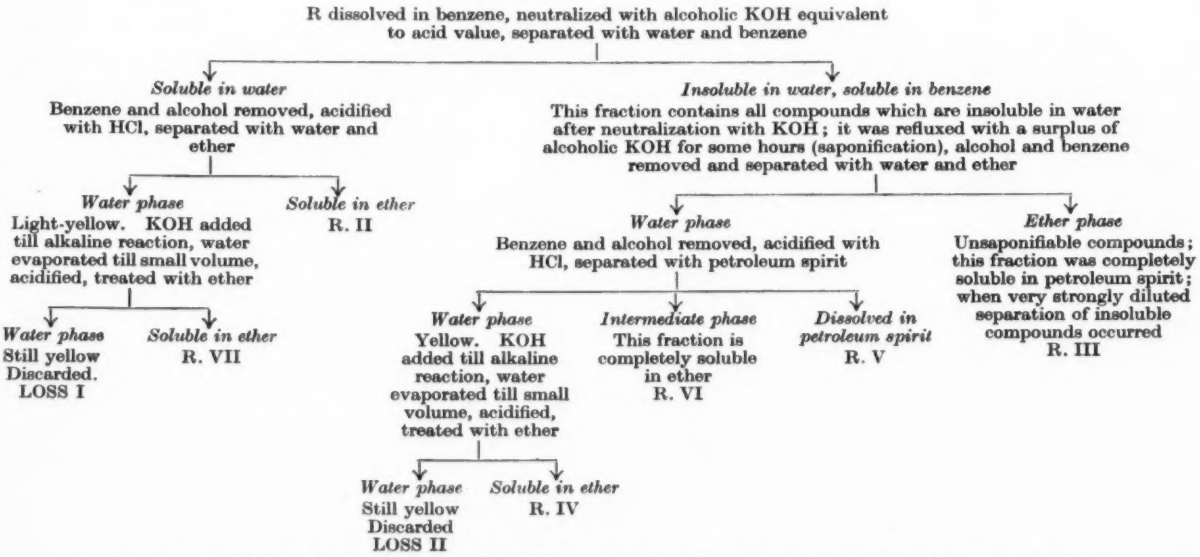

Oil dissolved in ether, neutralized with alcoholic KOH equivalent to acid value, separated with water and ether
Soluble in water
Ether and alcohol removed; acidified with HCl, separated with water and petroleum spirit 40–80°
Water phase
Strong odour of acetic acid
Discarded
LOSS I
Intermediate phase
Insoluble in either water or petroleum spirit, soluble in ether
WO. I; TO. I
Soluble in petroleum spirit
WO. II; TO. II
Insoluble in water, soluble in ether
Acidified with HCl and ether removed in order to determine LOSS I.
This fraction contains all compounds which are insoluble in water after neutralization with KOH.
Dissolved in benzene and refluxed with an excess of alcoholic KOH for some hours.
During this treatment the colour deepened considerably.
Alcohol and benzene removed and separated with water and ether
Water phase
Ether, benzene, and alcohol removed, acidified with HCl, separated with water and petroleum spirit
Ether phase
Acidified with HCl. This fraction is completely soluble in 40–60° petroleum spirit. When greatly diluted separation of insoluble compounds occurred again
WO. III; TO. III
Water phase
Colour pale-yellow; shaken with ether
Intermediate phase
Insoluble in either water or petroleum spirit
WO. VI; TO. VI
Soluble in petroleum spirit
Even after dilution with much petroleum spirit, insoluble material was again precipitated on further dilution
WO. V; TO. V
Water phase
Odour of acetic acid
Discarded
LOSS II
Dissolved in ether
Light yellow
WO. IV; TO. IV

Remarks.—Acid-treated fractions were freed from acid by water washing. Emulsified fractions were treated with Na Cl. Before removal of solvent the solution was dried with the aid of Na_2SO_4. Solvent was removed by evaporation below 40° C.

Solvent was removed by evaporation below 40° C.

FIG. 2.

METHOD OF WORKING UP THE "RESINS" R.


R dissolved in benzene, neutralized with alcoholic KOH equivalent to acid value, separated with water and benzene
Soluble in water
Benzene and alcohol removed, acidified with HCl, separated with water and ether
Water phase
Light-yellow. KOH added till alkaline reaction, water evaporated till small volume, acidified, treated with ether
Water phase
Still yellow
Discarded.
LOSS I
Soluble in ether
R. VII
Soluble in ether
R. II
Insoluble in water, soluble in benzene
This fraction contains all compounds which are insoluble in water after neutralization with KOH; it was refluxed with a surplus of alcoholic KOH for some hours (saponification), alcohol and benzene removed and separated with water and ether
Water phase
Benzene and alcohol removed, acidified with HCl, separated with petroleum spirit
Water phase
Yellow. KOH added till alkaline reaction, water evaporated till small volume, acidified, treated with ether
Water phase
Still yellow
Discarded
LOSS II
Soluble in ether
R. IV
Intermediate phase
This fraction is completely soluble in ether
R. VI
Dissolved in petroleum spirit
R. V
Ether phase
Unsaponifiable compounds; this fraction was completely soluble in petroleum spirit; when very strongly diluted separation of insoluble compounds occurred
R. III

Remarks.—The solubility of fractions R. IV and R. VII in ether is not reversible, otherwise remarks as given in Fig. 1.

TABLE II.

Composition of Oil WO *and Fractions.*

Fraction.	Fresh oil.	WO.	WO. I.	WO. II.	WO. III.	WO. IV.	WO. V.	WO. VI.	Loss I + Loss II + ordinary losses.
Mol. wt.	420	470	360	400	420	280	430	450	—
Determined in	Benzene	Benzene	Benzo-phenone	Benzo-phenone	Benzene	Benzo-phenone	Benzo-phenone	Benzo-phenone	—
Acid value, mg KOH/g	0	50	160	180	0	190	110	110	—
Ester value, mg KOH/g	0	50	70	30	0	—	40	50	—
Saponification No., mg KOH/g	0	100	230	210	0	—	150	160	—
Hydroxyl value, mg KOH/g	0	20	50	10	10	—	30	60	—
Carbonyl value, mg KOH/g	0	50	90	50	30	—	40	90	—
Peroxides, mg O_2/g	0	0·8	—	—	0·02	—	—	—	—
Viscosity at 20° C, cs	84	790	Syrupy	Highly viscous	254	Highly viscous	Highly viscous	Very tenacious	—
Percentage	—	100	10·4	5·9	56·3	0·5	10·1	2·3	5·0 + 9·5 = 14·5

TABLE III.

Composition of Oil TO *and Fractions.*

Fraction.	Fresh oil.	TO.	TO. I.	TO. II.	TO. III.	TO. IV.	TO. V.	TO. VI.	Loss I + Loss II + ordinary losses.
Mol. wt.	330	360	380	380	340	250	390	430	—
Determined in	Benzene	Benzene	Benzo-phenone	Benzo-phenone	Benzene	Benzo-phenone	Benzo-phenone	Benzo-phenone	—
Acid value, mg KOH/g	0	30	180	200	0	240	120	130	—
Ester value, mg KOH/g	0	40	100	40	0	—	50	60	—
Saponification No., mg KOH/g	0	70	280	240	0	—	170	190	—
Hydroxyl value, mg KOH/g	0	10	70	20	20	—	50	90	—
Carbonyl value, mg KOH/g	0	40	90	50	20	—	50	80	—
Peroxides, mg O_2/g	0	0·09	—	—	0·05	—	—	—	—
Viscosity at 20° C, cs	33	110	Syrupy	Highly viscous	54	Highly viscous	Highly viscous	Very tenacious	—
Percentage	—	100	6·4	4·4	67·8	0·6	6·9	2·1	2·7 + 9·1

TABLE IV.

Composition of "Resins."

Fraction.	"Resin" as such.	R. II.	R. III.	R. IV.	R. V.	R. VI.	R. VII.	Loss I + Loss II + ordinary losses.
Mol. wt.	380	370	330	? non-soluble	310	320	? non-soluble	—
Determined in	Dioxane	Benzophenone	Benzophenone	—	Benzophenone	Dioxane	—	—
Acid value, mg KOH/g	80	220	10	150	170	160	290	—
Ester value, mg KOH/g	200	140	0	110	—	80	—	—
Saponification No., mg KOH/g	280	360	10	260	—	240	—	—
Hydroxyl value, mg KOH/g	70	—	—	—	—	120	—	—
Carbonyl value, mg KOH/g	130	110	60	50	—	150	—	—
Consistency	Tenacious	Syrupy	Highly viscous, somewhat syrupy	Highly viscous, semi-solid	Highly viscous, somewhat syrupy	Lacquery	Highly viscous, somewhat syrupy	—
Percentage	100	14·8	8·3	11·1	3·1	50·8	7·9	4·0

Discussion.

It should be noted that WO is in a more advanced state of oxidation than TO, so that the fact that " resins " precipitate from oxidized white oil but not from oxidized transformer oil cannot be attributed to a lower degree of oxidation of the former. Apparently the phenomenon being dealt with is closely related to the constitution of the oil itself.

The close resemblance of Tables II and III is noteworthy. The close relationship of those fractions which have the same denominator is quite understandable, as both oils are worked up according to the same scheme. However, it is striking that the ratios of the fractions of both oils are practically the same. This was not to be expected for two oils so different in their susceptibility to the addition of glass and in the precipitation of " resins " during oxidation.

From the analyses it appears that mineral-oil-oxidation products are complicated compounds containing several active groups per molecule. The fractions are not pure substances and may be made up of related compounds containing more or less groups per molecule. It is reasonable to conclude from the tables that the oxidation products contain generally several different polar groups per molecule. This means that, during fractionation, according to our scheme, different oxidation products which otherwise show a striking similarity (all oxidation products are carbonyl-containing hydroxy acids and their anhydrides *) accumulate in one fraction or another according to a relative predominance of certain typical groups.

The " resins " are also carbonyl-containing hydroxy acids and their anhydrides, but their carbonyl value is somewhat higher than that for the oxidation products which do not precipitate. Possibly there is some relationship between TO. I and R, for both have approximately the same analysis and molecular weight.

As to why insoluble carbonyl-containing hydroxy acids precipitate from oxidized transformer oil but remain dissolved in white oil, this may be attributed to the presence of aromatic rings in the transformer-oil-oxidation products. From the constitution of the two oils (Table I) the presence of aromatic rings is probable in the oxidation products of transformer oil, but not in those products of white oil.

How this may account for differences in solubility and in oxidizability is a subject for further study.

The most remarkable fact which emerges from this investigation is the constancy of the molecular weights of all oxidation products. The molecular weight of all fractions is about the same as that of the fresh oil. While some fractions show a higher molecular weight due to the taking-up of oxygen, others are of lower molecular weight on account of some splitting off of side chains. The general trend, however, is to constancy of molecular weight, R, and its fractions included. This was not expected

* Hydroxy acids, their derivatives, and their anhydrides are soluble in ethyl alcohol. As practically all oxidation products are hydroxy acids, a fair indication of the degree of oxidation of a mineral oil can be obtained by shaking it with 96 per cent alcohol and recovering the dissolved fraction. Thus, from the oils used in this investigation a 50 to 60 per cent yield of extract was obtained.

with insoluble resin-like substances rich in carbonyl groups with high ester value.

At first it was wondered what ester value indicated. As acetic and other lower acids are formed during mineral-oil oxidation it is not impossible that these were esterified by the hydroxyl groups of larger molecules. If this were so, large quantities of acids should be found after saponification, but, although lower acids were detected, their quantity was too small to explain the magnitude of the ester value.

It was then recalled that hydroxy acids tend to form internal anhydrides, a process which occurs more easily at higher temperatures. As the oxidation tests were made at 140° C this might be the origin of the ester value. When anhydrides are formed the acid value decreases. Therefore fraction WO.V was heated and the acid value determined. The results given in Table V confirm this opinion.

TABLE V.

	Acid value, mg. KOH/g.	Consistency.
WO. V as such	110	High-viscosity oil
After 20 hr at 105° C . . .	100	↓
After further 7 hr at 120 ° C .	60	Syrupy

In order to discuss the viscosity of the oils during oxidation reference is made to Table VI.

TABLE VI.

	Viscosity at 20° C, cs.	
	White oil.	Transformer oil.
Fresh oil	84	33
After oxidation (WO and TO) .	789	110
WO. III and TO. III * . .	407	73

* WO and TO after removal respectively of 43·7 and 32·3 per cent of the oxidized oil.

Taking into account the molecular weights of the respective fractions, it appears from Table VI that viscosity increase is not due to increase in molecular weight but to the appearance of polar groups in the molecule. The percentage decrease in viscosity (after the removal of known percentages of oxidized compounds), together with the chemical composition of both the fractions removed and of the residues (WO. III and TO. III), point to a predominant influence on viscosity of the carbonyl groups. This confirms the statement made in the previous paper that a relationship must exist between carbonyl groups and viscosity.

These experiments were done in the laboratory with very special oils. When a series of used lubricating oils from bench tests in an aircraft engine became available, their acid, ester, and carbonyl values were determined.

These values, which show some relationship between laboratory experiments and practice, are given in Fig. 3.

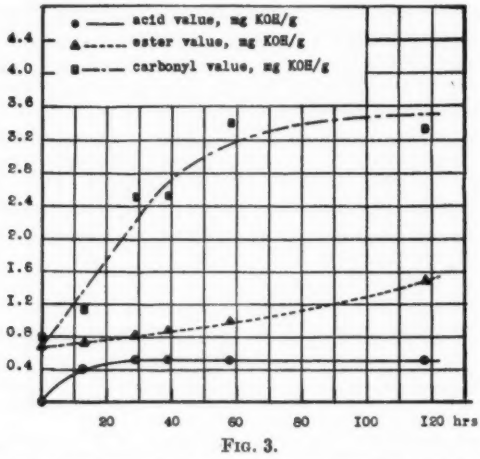


FIG. 3.

DETERIORATION OF LUBRICATING OIL IN AIRCRAFT ENGINE DURING BENCH TEST.

ACKNOWLEDGMENTS.

The authors wish to express their sincere thanks to Dr S. H. Bertram, director of the "Nederlandsche Research Centrale," to whose extensive knowledge of organic chemistry they have never appealed in vain. They also desire to acknowledge their indebtedness to the Motor Dept. of the Royal Dutch Air Lines for permission to mention the experiments reported in Fig. 3.

ON THE PROPERTIES OF PARAFFIN WAX IN THE SOLID STATE.

By W. M. Mazee.*

Summary.

A description is given of the behaviour of some binary mixtures of pure hydrocarbons. It was found that a n-$C_{21}H_{44}$ and a n-$C_{22}H_{46}$ form a continuous series of mixed crystals, whereas n-$C_{21}H_{44}$ and n-$C_{31}H_{64}$ form a eutectic so that n-$C_{21}H_{44}$ and n-$C_{31}H_{64}$ crystallize separately. A mixture of n-$C_{24}H_{50}$ and 13-methylpentacosane also gave a binary system with a eutectic. On the strength of these phenomena a hypothesis was formulated on the structure of commercial paraffin waxes.

Introduction.

Minchin [1] gives an interesting account of the properties of paraffin waxes in the solid state, and propounds a hypothesis concerning the solidification of paraffin wax and the state in which the solid wax might be at room temperature.

The present information may serve as a completion of the facts already known and thus contribute towards a better understanding of the constitution of paraffin wax.

Investigations were made with a number of synthetic pure hydrocarbons, the properties of which have been published elsewhere.[2]

Behaviour of some Binary Mixtures.

Some binary mixtures of the pure hydrocarbons were prepared and a temperature–time curve obtained as follows :—

A polished silver vessel, diameter 1·8 cm, height 2 cm, filled with gilt nickel gauze, was placed in a round-bottom flask with ground-glass stopper. A thermometer passed through the stopper so that the bulb was in an opening in the nickel gauze, in the centre of the silver vessel. A second opening in the stopper was connected with a tube containing solid sodium hydroxide. The flask itself also contained some pellets of solid sodium hydroxide to keep the surface of the silver vessel bright for a long time.

The vessel was filled with the substance to be examined and then replaced in the flask, after which the latter was placed in a thermostat tank containing vigorously stirred water.

The water-bath was heated by maintaining a constant difference between the temperature of the water-bath and that registered by the thermometer in the silver vessel. In this way heat transmission to the silver vessel was kept constant so that comparable results were obtained. For further details we refer to other publications.[3]

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(a) n-*Heneicosane and* n-*Tricosane.*

The first binary system investigated was *n*-heneicosane and *n*-tricosane ($C_{21}H_{44}$ and $C_{23}H_{48}$). The melting curve for this system was calculated both for the case when a eutectic would be formed, and the case when the two components would form a continuous series of mixed crystals. It was in both cases assumed that the mixture behaved as an ideal mixture; so no mixing heat and no change of volume was assumed. The calculation of the melting curve from Raoult's equation in the case of an eutectic is well known :—

$\ln(1-x) = \frac{Q}{R}\left(\frac{1}{Tm} - \frac{1}{T}\right)$ in which x = mol fraction component, Tm = melting temperature of component, T = temperature at which component begins to crystallize, Q = molal heat of fusion, R = gas constant.

The molal heat of fusion of *n*-$C_{21}H_{44}$ is 16·9 k.cal and of *n*-$C_{23}H_{48}$ is 19·4 k.cal.

The calculation of the temperature at which the last traces of mixed crystals just become liquid, and the temperature at which the first liquid appears is as follows :—

In a mixture consisting of x_1 mol per cent of the first component, melting point $T_1°$, molal heat of fusion Q_1 cal and of $1 - x_1$ mol % $= x_2$ mol % second component, melting point $T_2°$ and molal heat of fusion Q_2 cal, the last traces of solid mixed crystals disappear at a temperature T. In general Raoult's equation gives

$$\ln \frac{x_{1l}}{x_{1s}} = \frac{Q_1}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which x_{1l} is the composition of the liquid and x_{1s} the composition of the solid.

Introducing e equation (1) passes into equation (2)

$$x_{1s} = x_{1l}\, e^{\frac{Q_1}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The same equation applies for the second component

$$x_{2s} = x_{2l}\, e^{\frac{Q_2}{R}\left(\frac{1}{T} - \frac{1}{T_2}\right)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

As $x_{1s} + x_{2s} = 1$ equations (2) and (3) can be combined

$$x_{1l}\, e^{\frac{Q_1}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)} + x_{2l}\, e^{\frac{Q_2}{R}\left(\frac{1}{T} - \frac{1}{T_2}\right)} = 1 \quad . \quad . \quad . \quad . \quad (4)$$

The temperature T, at which the mixture is just liquid can be calculated from equation (4).

On the analogy of the preceding, the temperature T_3 at which the first traces of liquid appear can be calculated from the following equation :—

$$x_{1s}\, e^{\frac{Q_1}{R}\left(\frac{1}{T_3} - \frac{1}{T_1}\right)} + x_{2s} e^{\frac{Q_2}{R}\left(\frac{1}{T_3} - \frac{1}{T_2}\right)} = 1.$$

Some of the results obtained are shown in Table I.

TABLE I.

Observed and Calculated Values of Initial and Final Melting Points in the System n-$C_{21}H_{44}$–n-$C_{23}H_{48}$.

Mixture.	Observed.		Calculated.			
			Eutectic.		Mixed crystals.	
	Initial melting point, ° C.	Final melting point, ° C.	Eutectic temp. ° C.	Final melting point, ° C.	Initial melting point, ° C.	Final melting point, ° C.
50 mol % n-$C_{21}H_{44}$ + 50 mol % n-$C_{23}H_{48}$	43·1	44·4	36	40·3	43·6	44·7
80 mol % n-$C_{21}H_{44}$ + 20 mol % n-$C_{23}H_{48}$	41·6	42·2	36	38	41·6	42·4

This table shows that the occurrence of a eutectic is out of the question; neither does the temperature–time curve indicate a constant temperature which should have been so in the case of a eutectic (Fig. 1). There is a reasonable agreement in the formation of a continuous series of mixed crystals. A better agreement can hardly be expected, as the composition

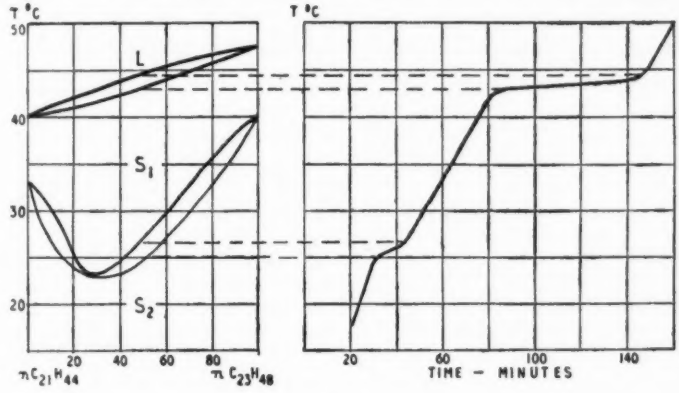

FIG. 1.

THE SYSTEM n-$C_{21}H_{44}$ TO n-$C_{23}H_{48}$.

of the mixed crystals that deposit first will not be quite the same as that of the mixed crystals depositing later. The pronounced drop in transition point observed for the mixtures also indicates formation of mixed crystals. For the equimolecular mixtures a transition range of 25° to 26° C was found, the transition point for the pure components being 32·8° C and 40·6° C, respectively. Microscopical observations of various mixtures showed that the minimum in the transition temperature (the mixture consisting of about 25 mol per cent $nC_{21}H_{44}$) occurs at a temperature of about 23° C. The T–x diagram then assumes the shape shown in Fig. 1.

It is clear from these experiments that despite a slight difference in chain length, hydrocarbon molecules can still crystallize as one crystal. Thus, instead of a well-defined melting point a melting range occurs, whose temperature limits lie above the melting point of the lowest melting component and below that of the highest melting component. There is also a transition zone instead of a well-defined transition point. The transition point of each of the hydrocarbons is lowered by the addition of the other component. The temperature difference between transition range and melting range of a mixture is therefore greater than in the case of the pure components.

n-*Heneicosane and* n-*Hentriacontane*.

The second system investigated was a series of mixtures of *n*-heneicosane and *n*-hentriacontane ($C_{21}H_{44}$ and $C_{31}H_{64}$).

The melting curves of this system, too, were calculated from the experimentally determined total heat of fusion of the two components for the case that a eutectic would be formed, on the assumption that no mixing heat would be generated and no change in volume would take place. The molal heat of fusion of n-$C_{31}H_{64}$ is 23·9 k.cal. The eutectic would be formed at a composition of 96 mol per cent of n-$C_{21}H_{44}$ and 4 mol per cent of n-$C_{31}H_{64}$ and a temperature of 40° C. The relevant observations and calculations are collected in Table II.

TABLE II.

Calculated and Observed Values of Initial and Final Melting Points in the System n-$C_{21}H_{44}$–n-$C_{31}H_{64}$.

Mixture.	Observed.		Calculated.	
	Initial melting point, ° C.	Final melting point, ° C.	Initial melting point, ° C.	Final melting point, ° C.
75 mol % n-$C_{21}H_{44}$ + 25 mol % n-$C_{31}H_{64}$	40	54·6	40	55·1
50 mol % n-$C_{21}H_{44}$ + 50 mol % n-$C_{31}H_{64}$	40	61·0	40	61·1
25 mol % n-$C_{21}H_{44}$ + 75 mol % n-$C_{31}H_{64}$	40	64·8	40	64·7

The calculated and observed temperatures are in good agreement. Fig 2 in addition to the T–x diagram shows the temperature–time curves of two of the mixtures examined. In these cases the transition temperature has practically not been lowered, which makes it probable that miscibility does not occur in the solid state either. The transition temperature of the mixture is 32·4° to 32·7° C, that of pure n-$C_{21}H_{44}$ being 32·8° C.

If the melt of a mixture composed of, say, 40 mol per cent n-$C_{31}H_{64}$ and 60 mol per cent n-$C_{21}H_{44}$, is cooled down, pure n-$C_{31}H_{64}$ begins to crystallize at 59° C, *i.e.*, point A in Fig. 2. On further cooling the quantity of n-$C_{31}H_{64}$ crystallizing gradually increases, the remaining liquid becoming gradually richer in n-$C_{21}H_{44}$. The composition of the liquid depends on the slope and the position of the melting-curve. At the eutectic temperature, *i.e.*, at 40° C, n-$C_{21}H_{44}$ also begins to crystallize. When all liquid has disappeared one has arrived at the temperature zone in which solid n-$C_{21}H_{44}$ and solid $C_{31}H_{64}$ occur side by side.

n-Tetracosane and 13-Methylpentacosane.

The third binary system investigated was a mixture of a normal hydrocarbon with 24 carbon atoms and a branched hydrocarbon with 26 carbon atoms, viz., *n*-tetracosane and 13-methylpentacosane.

In this case, too, the melting curves were calculated. The molal heat of fusion of n-$C_{24}H_{50}$ is 20·5 k.cal, that of 13-methylpentacosane is 17·1 k.cal. There appeared a eutectic at a composition of 8·5 mol per cent *n*-tetracosane and 91·5 mol per cent 13-methylpentacosane and at a temperature of 28° C.

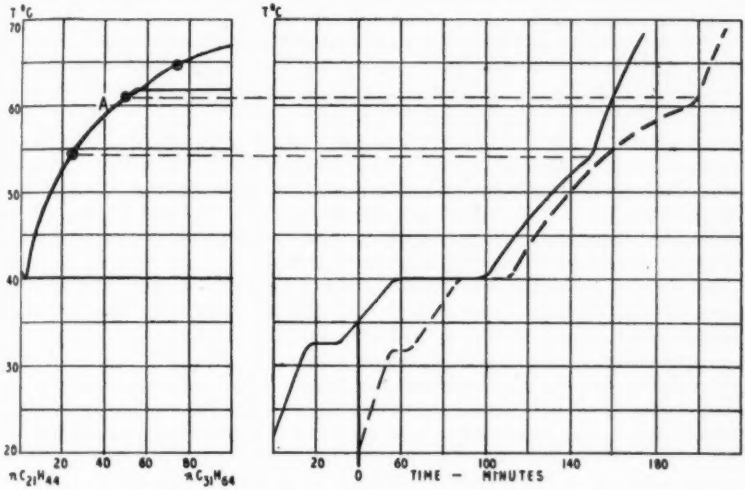

FIG 2.

THE SYSTEM n-$C_{21}H_{44}$ TO n-$C_{31}H_{64}$.

Only one mixture consisting of 50 mol per cent tetracosane and 50 mol per cent 13-methylpentacosane was examined in the silver vessel. The eutectic temperature was found at 28° C, the temperature at which the last traces of solid substance disappeared was 43·5° C, the calculated temperature being 43·9° C. A mixture of 25 mol per cent *n*-tetracosane and 75 mol per cent 13-methylpentacosane was heated slowly in a capillary, which was observed with a powerful lens. Initial melting occurred at 28° C (which corresponds with the eutectic temperature) and the final melting point at 37·6° C, the calculated value for the final melting point being 37·4° C.

The observed and calculated values are in satisfactory agreement. In this case, too, no-mixed crystals were formed; the two components will, therefore, crystallize separately.

A Hypothesis on the Structure of Solid Paraffin Wax.

Viewed in the light of the above experiments, the structure of the commercial paraffin waxes might be interpreted by the following hypothesis.

The normal hydrocarbons occurring in a wax from about $C_{21}H_{44}$ to

$C_{34}H_{70}$, are capable of forming mixed crystals in small groups, *e.g.*, $C_{34}H_{70}$ with $C_{33}H_{68}$ and $C_{32}H_{66}$; but in their turn $C_{33}H_{68}$ and $C_{32}H_{66}$ are liable to form mixed crystals with the two next hydrocarbons.

The "soft wax", *iso*- and *cyclo*paraffins, crystallize by the side of the mixed crystals; possibly they constitute a "lubricating film" between the mixed crystals.

As by the formation of mixed crystals the transition point of pure hydrocarbons is considerably lowered, it is possible that part of the waxes is invariably present in the modification that is stable immediately below the melting point.

Further, an exact transition temperature cannot be expected in these cases, but a transition zone which, owing to the large number of components, will extend over a still greater temperature range than in the case of the binary mixture of n-$C_{21}H_{44}$ and n-$C_{23}H_{48}$.

Consequently, the transition heat will be distributed over a greater temperature range and it is conceivable that when a temperature–time curve is drawn there is no longer discontinuity in the heating curve of the solid substance. But in this case the slope of the line will be less steep, which means that a high specific heat of the solid substance is measured. This is an apparent specific heat representing the actual specific heat increased by a transformation heat which is distributed over a certain temperature range. This explains the fact mentioned by Minchin and observed by others[3] that a value of about 40 cal/g is found for the specific heat of fusion of a commercial wax, whereas the value of the specific heat of fusion of the modification of the pure hydrocarbons, which is stable at low temperature, is about 58 cal/g. The difference between these two values constitutes the transformation heat which, if measured direct on the pure hydrocarbons, is indeed of the order of 12 to 20 cal/g.[2] In this way one arrives at a hypothesis on the structure of commercial paraffin wax that may explain different properties.

Amsterdam.
May 1948.

References.

[1] Minchin, S. T. *J. Inst. Petrol.*, 1948, **34**, 541.
[2] Mazee, W. M. *Rec. Trav. Chim.*, 1948, **67**, 197.
[3] Sullivan, F. W., McGill, W. I., and French, A. *Industr. Engng Chem.*, 1927, **19**, 1040; Kozicki and Pilat. *Petroleum*, 1918, **14**, 12; Lord, H. D., *J. Inst. Petrol.*, 1939, **25**, 263.

ALKYLNAPHTHALENES. PART III. THE *n*-BUTYL-AMYL- AND HEXYLNAPHTHALENES.

By A. S. Bailey, G. B. Pickering, and J. C. Smith (Fellow).

The six hydrocarbons here described form, along with those of Part II[1] of this series of papers, a set of homologues in which the strongly aromatic character of naphthalene is in many respects diminished as the aliphatic proportion of the molecule increases.

For the β-alkylnaphthalenes the best method of preparation is through the corresponding β-naphthyl-*n*-alkyl ketones, which are easily purified, highly crystalline substances; for the α-isomerides a variety of methods has been explored, and the Wurtz–Fittig reaction between α-bromonaphthalene and the alkyl bromides found to be the least troublesome. Purification of the hydrocarbons through the molecular complexes with aromatic polynitro-compounds becomes more difficult as the homologous series is ascended, and has not been found satisfactory above the ethylnaphthalenes. Styphnates are obtained only with the methyl- and ethylnaphthalenes; picrates of the *n*-propyl and butyl homologues are obtainable but rather unstable; *s*-trinitrobenzene complexes are stable (except that from α-*n*-butyl) right up to the amylnaphthalenes. There is thus a gradation of reagents for complex formation (*s*-trinitrobenzene being more powerful than picric acid which in turn is more powerful than styphnic acid) and a similar gradation in the hydrocarbons from methyl- to hexylnaphthalenes. There seems to be little difference in stability between complexes from the α- and those from the β-series. For the methyl- and ethyl-naphthalenes the six complexes obtainable from the α-hydrocarbons are all higher-melting than the corresponding complexes from the β-isomers. This regularity does not hold higher up the series.

As regards the physical properties of the hydrocarbons themselves there are some interesting differences between the α- and the β-series. Melting points, being properties of the solid state, are influenced by many factors, and it is difficult to draw conclusions from the values shown in Fig. 1, but the melting points would be expected to show an upward trend when the alkyl chain became long enough to impose its characteristics. Dr B. Elsner and Mr B. Bannister, of this laboratory, report that β-*n*-octylnaphthalene and β-*n*-decylnaphthalene melt at 10° and 19°, respectively (private communication), so that, in the β-series, the rise in melting point begins approximately with the C_6 side chain. The boiling points, of course, show a general rise with increase in molecular weight, but there is an unexpected crossing of the curves: at first the α-compounds have the higher boiling points, but at *n*-propylnaphthalene the β-isomer becomes the higher-boiling and the β-curve continues above the α-curve.

Refractive indices fall on two curves, the higher values belonging to the α-series. At least as far as the *n*-hexylnaphthalenes the refractive index *decreases* with increasing molecular weight because of the increasing

proportion of aliphatic nature in the molecule. Similarly, the densities fall on two distinct curves, the α-isomers being the denser; α-methyl- and α-ethylnaphthalene are actually heavier than water.

The exaltations of molecular refraction (2·5—2·9 for the α-series, and 2·9—3·3 for the β-series) and of specific refraction (1·3—1·9) are in close agreement with the values found by von Auwers [2] for naphthalene, α- and β-methylnaphthalene, and some dimethylnaphthalenes.

Preliminary results for the specific dispersions show little difference

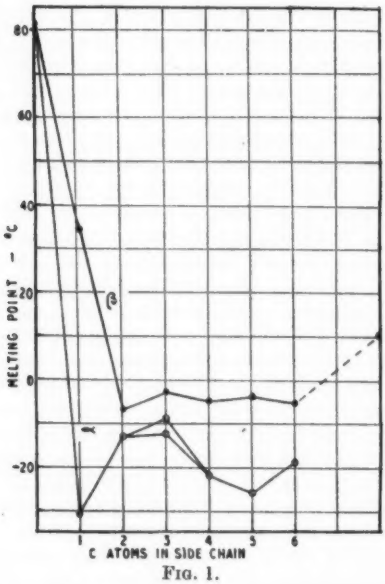

FIG. 1.

between the α- and β-series, but of course there is a large drop in dispersion as the aliphatic portion increases. If higher alkylnaphthalenes (or benzenes) are present in a mixture this type of change must be borne in mind when the measurement of specific dispersion is used for analysis [2a] of mixtures of aromatics, olefins, and paraffins.

Melting Points of the molecular complexes were taken in capillary tubes in the usual way. For the hydrocarbons themselves a portion of 5 to 10 cc in a long tube was cooled until partly frozen, with a toluene thermometer in the liquid. The tube was then placed in cotton wool and allowed to warm slowly, a long arrest occurring at the melting point. Temperatures were correct to $\pm 1°$.

Boiling Points were obtained by slow distillation of the hydrocarbon from a small flask with a column attached and an insulated head. Short-stem Anschütz thermometers were used, and, when substances were being compared, they were distilled under the same conditions from the same apparatus.

Densities. Two pycnometers of capacity 0·7 cc and 7·5 cc respectively were used, and in several tests they gave densities agreeing to three decimal places. (In some cases only small amounts—less than 1 g—of hydrocarbon remained for the determination, after other needs had been met.)

Refractive Indices were determined on the Abbé instrument, care being

TABLE I.

n-Alkylnaphthalenes.

Homologue.	M.p., °C.	B.p., °C/760 mm.	D_4^{20}.	n_D^{20}.	$[R_L]_D$.	EM_D.	$E\Sigma_D$.	$\frac{(n_F - n_c)}{d} \times 10^4$.
α-Me	−31	244·5	1·020	1·6174	48·80	2·53	1·78	285
β-Me	+34·3	241	—	—	—	—	—	—
α-Et	−13·5	259	1·008	1·6062	53·47	2·58	1·65	270
β-Et	−7	258	0·992	1·5999	53·86	2·97	1·90	270
α-*n*-Pr	−13 and −9	272·5	0·990	1·5923	58·20	2·70	1·59	259
β-*n*-Pr	−3	273·5	0·977	1·5872	58·60	3·10	1·81	258
α-*n*-Bu	−22	289	0·977	1·5811	62·87	2·75	1·49	248
β-*n*-Bu	−5	292	0·966	1·5776	63·27	3·15	1·70	249
α-*n*-Amyl	−26	307	0·966	1·5728	67·62	2·88	1·33	240
β-*n*-Amyl	−4	310	0·956	1·5694	67·99	3·25	1·64	240
α-*n*-Hexyl	−18	322	0·958	1·5652	72·21	2·86	1·35	229
β-*n*-Hexyl	−5·5	323·5	0·948	1·5620	72·63	3·28	1·45	230

TABLE II.

n-Alkylnaphthalene Complexes.

Alkylnaphthalene.	Styphnate, m.p.	Picrate, m.p.	T.N.B. complex, m. p.
α-Me	134–135°	141·5°	153·5–154·5°
β-Me	129·5°	116–117°	124°
α-Et	111–113° (decomp.)	99°	111·5–112°
β-Et	88–90° (decomp.)	77°	87–88°
α-*n*-Pr	—	84–86°	86–87°
β-*n*-Pr	—	90°	99°
α-*n*-Bu	—	64° (decomp.)	70–71° (decomp.)
β-*n*-Bu	—	63–65° (decomp.)	76°
α-*n*-Amyl	—	—	75°
β-*n*-Amyl	—	—	74°
α-*n*-Hexyl	—	—	69–74° (decomp.)
β-*n*-Hexyl	—	—	67–68° (decomp.)

taken to maintain the prisms at 20° ± 0·1°, and the instrument was frequently checked against the standards. When our Abbé instrument was not available the specific dispersions, $\frac{(n_F - n_c)}{d} \times 10^4$, were kindly determined by Mr G. T. Kennedy at King's Langley.

Molecular Refractions, Molecular Exaltations, and Specific Exaltations, calculated from the Lorenz–Lorentz equation, are included in Table I.

In Table I the values of physical constants given for the methyl, ethyl, and *n*-propylnaphthalenes are those already communicated in Part II [1] of this series.

In the figures, when values for naphthalene itself are shown, they are those usually quoted in the literature.

1- AND 2-*n*-BUTYLNAPHTHALENES.

Bargellini and Melacini [3] prepared the two naphthyl-*n*-propyl ketones by the Friedel–Crafts reaction in carbon disulphide solution and claimed to have separated them by means of the picrates, that of the β-compound being the less soluble. Reduction by prolonged boiling in aqueous suspension with iodine and phosphorus gave the hydrocarbons, 1-*n*-butyl-

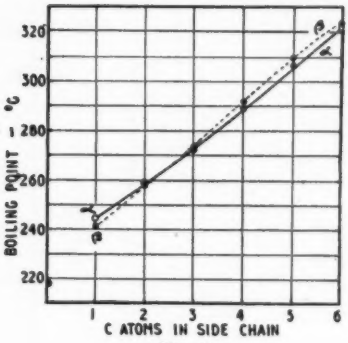

FIG. 2.

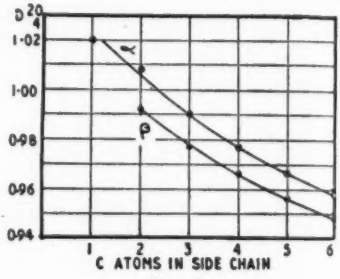

FIG. 3.

naphthalene boiling at 281° to 283° and yielding a picrate of m.p. 104° to 106°; the 2-isomeride boiled at 283° to 284°, and its picrate melted at 71° to 74°.

Petrov and Andreev [4] allowed *n*-butyl chloride to act on naphthalene (in presence of aluminium chloride) in cold *cyclo*hexane solution. For 2-*n*-butylnaphthalene they recorded b.p. 282·5° to 283·5°, f.p. — 53°, and n_D^{20} 1·5790 : their product was probably a mixture of α- and β-compounds with branched, as well as normal, side-chains.

In this investigation it was found that the product of the Friedel–Crafts reaction, even when carbon disulphide was the solvent, contained sufficient of the 2-naphthyl-*n*-propyl ketone for this to crystallize from the mixture : use of the picrate was found unnecessary and inefficient. From the ketone, 2-*n*-butylnaphthalene was readily obtained by the modified Wolff–Kishner reduction. The picrate, m.p. 63° to 65°, was rather unstable, but the *s*-trinitrobenzene complex was suitable for identification.

It was not found possible to purify the residual 1-naphthyl-*n*-propyl ketone through either its picrate or its semicarbazone. Bargellini and Melacini [3] claimed that, for the hydrocarbons, the picrate of the α-compound was the higher-melting. Accordingly our crude α-ketone was reduced and the product combined with picric acid : the picrate obtained melted over a range of 20° and was too unstable for purification.

It seemed advisable to obtain the α-*n*-butylnaphthalene by a method which avoided the mixture of ketones, and recourse was had to the Fittig reaction between *n*-butyl bromide and α-bromonaphthalene. (This

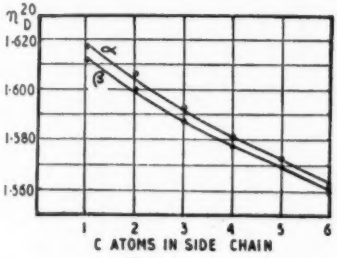

FIG. 4.

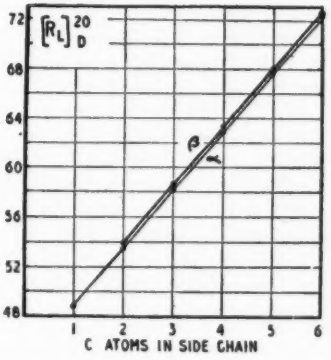

FIG. 5.

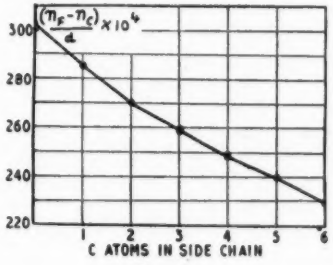

FIG. 6.

α-halogen compound was relatively easily freed from the β-isomeride.[5] Three hydrocarbons were produced in the reaction; nevertheless, a separation was possible. Benzene was used as solvent, but later experiments with *n*-amyl bromide showed that in ether the reaction was more readily controlled and higher yields of hydrocarbon were obtained.

EXPERIMENTAL.

1-n-*Butylnaphthalene.*

α-Bromonaphthalene was distilled, first at atmospheric pressure (b.p. 280°) in order to decompose naphthalene dibromide; then at 15 mm (b.p. 146° to 147°) with a column. The distillate was crystallized in batches of 60 cc from absolute ethyl alcohol (200 cc) at — 15° in order to remove β-bromonaphthalene. The best preparation melted at 6·1°. (Jones and Lapworth [5] give m.p. 6·2°.)

Sodium (35 g, 1·5 g atoms) in thin slices was placed below dry benzene

(70 cc) in a 700-cc reflux apparatus. While the flask was warmed in an oil-bath a mixture of pure *n*-butyl bromide (68·5 g, 0·5 mole, b.p. 116° to 117°, n_D^{20} 1·4396) and α-bromonaphthalene (80 g, 0·39 mole, m.p. 5° to 6°) was added in portions of 15 cc. The temperature was kept at about 80° (and should not exceed 90°) during the addition and for 2 hr afterwards. Distillation at 10 mm gave first some octane, then naphthalene, and finally the butylnaphthalene; possibly there was some dinaphthyl in the small residue. Redistillation gave 24·3 g of still impure hydrocarbon boiling at 150° to 165° at 22 mm and yielding fractions, the refractive indices of which fell from 1·600 to 1·592 as the b.p. rose : these fractions all contained halogen. They were therefore recombined and stirred with sodium at 180° for 10 min, then for 3 min at 225°; the liquid, distilled from the sodium at 157° to 158° at 20 mm. had n_D^{20} 1·582. Repetition of the treatment with sodium gave a product boiling at 157° at 20 mm with n_D^{20} 1·5811, free from halogen and unchanged by further treatment with sodium. It boiled at 289° (corr) at 752 mm and melted at − 23°; the yield was only 8 g. (Found : C, 91·3; H, 8·7 per cent. Calc. for $C_{14}H_{16}$ C, 91·3; H, 8·7 per cent.) Use of ether instead of benzene as solvent would probably raise the yield of this hydrocarbon as was found for the amyl homologue.

Molecular Compounds. The hydrocarbon (0·5 g, 1 mol) and picric acid (0·42 g, 0·67 mol) dissolved in ethyl alcohol (6 cc) deposited yellow needles melting, with obvious decomposition, at 64°. (Found : N, 10·4 per cent. Calc. for $C_{14}H_{16}{\cdot}C_6H_3O_7N_3$: N, 10·1 per cent.) It was necessary to use excess of the hydrocarbon in this preparation. Bargellini and Melacini [3] gave 104° to 106° as the m.p. of this picrate.

Equivalent quantities of the hydrocarbon and of *s*-trinitrobenzene, mixed in alcoholic solution, gave fine yellow needles, m.p. 70° to 72°, but these were not homogeneous. (Found : N, 12·6 per cent. $C_{14}H_{16}{\cdot}C_6H_3O_6N_3$ requires N, 10·6 per cent.) As the complex appeared to be unstable in presence of alcohol it was prepared by mixing and fusing weighed equivalent quantities of the components : the yellow solid melted at 69° to 71°.

2-n-Butylnaphthalene.

Thionyl chloride was purified by heating under reflux for several hours with 1 per cent of sulphur and then distilling. Pure butyric acid (141 g, 1·6 mole, b.p. 162° to 163°) and thionyl chloride (204 g, 1·88 mole) yielded 141 g (83 per cent) of butyryl chloride, b.p. 101°.

α- and β-Naphthyl-n-Propyl Ketones.

To a cold, stirred solution of naphthalene (128 g, 1 mole) and butyryl chloride (117 g, 1·1 mole) in carbon disulphide (500 cc) powdered aluminium chloride (160 g, 1·2 mole) was added gradually so that the temperature remained below 5°. The reaction mixture was poured into excess of dilute hydrochloric acid containing ice. From the carbon disulphide layer, after this had been thoroughly washed and dried, distillation at 128° at 30 mm gave naphthalene (45 g), and the mixture of ketones passed over at 208° at 30 mm (88 g, 68 per cent yield calculated on the naphthalene used up). This mixture partly crystallized on standing. The crystals removed by filtration were washed with alcohol and then dried; the alcoholic washings were added to the filtrate and the liquid, cooled in a freezing-

mixture, gave successive crops (total 44 g) of the solid ketone. (Distillation of the new filtrate gave 42 g of oil containing, presumably, much α-ketone.) After one crystallization from alcohol the β-ketone melted at 53° to 54°, unchanged by further crystallization. (Literature,[6] 53°.)

2-n-*Butylnaphthalene.*

The ketone was reduced by the modified Wolff–Kishner method[7] (heating in diethylene-glycol solution with hydrazine and sodiodiethylene glycollate). Sodium (2·5 g) was dissolved in diethylene glycol (70 cc) in a 100-cc reflux apparatus. The ketone (10 g), hydrazine hydrate (5 cc of 85 per cent) were added, and the mixture heated 1 hr under reflux. Heating then without the condenser allowed water to escape until the temperature reached 195°. With an air-condenser attached, the flask was then heated for 3 hr. On cooling, the mixture separated into hydrocarbon and glycol layers. Water was added and the whole was extracted with several portions of petroleum ether (100 cc total); the extract was washed with water, dil hydrochloric acid, with water again, and then dried. It gave a yellow oil (8·9 g, 95 per cent yield) which distilled at 150° at 14 mm; n_D^{20} 1·5776. Redistillation with a small column gave a main fraction of b.p. 156° to 157° at 21 mm, 291·5° at 752 mm, m.p. − 5°, n_D^{20} 1·5776. (Found: C, 91·3; H, 8·8 per cent. $C_{14}H_{16}$ requires C, 91·3; H, 8·7 per cent.)

Molecular Compounds. An attempt to prepare the picrate using equivalent quantities of the hydrocarbon and picric acid gave a product melting at 62° to 110° (containing uncombined picric acid). When the hydrocarbon (0·6 g, 1 mol) and picric acid (0·5 g, 0·66 mol) were dissolved in 4 cc of ethyl alcohol, a yellow picrate, m.p. 63° to 65°, separated. (Found: N, 10·0 per cent. Calc. for $C_{14}H_{16}{\cdot}C_6H_3O_7N_3$: N, 10·2 per cent.) Bargellini and Melacini[3] stated that the picrate melted at 71° to 74°.

The hydrocarbon and *s*-trinitrobenzene (equivalent quantities) dissolved in ethyl alcohol gave thin yellow needles of the complex, m.p. 76°. (Found: N, 10·7 per cent. $C_{14}H_{16}{\cdot}C_6H_3O_6N_3$ requires N, 10·6 per cent.)

1- AND 2-*n*-AMYLNAPHTHALENE.

The *n*-amylnaphthalenes seem not previously to have been prepared. Accounts of amylnaphthalenes in the literature[8] refer to *tertiary*-amylnaphthalenes made commercially by the Friedel–Crafts alkylation of naphthalene.

In this investigation 1-*n*-amylnaphthalene was made by the Wurtz–Fittig reaction between pure 1-bromonaphthalene and *n*-amyl bromide. From the resulting mixture the pure amylnaphthalene was separated readily in 45 per cent yield. Another route, condensation of α-tetralone with *n*-amylmagnesium bromide, followed by dehydration and dehydrogenation, led to products difficult to purify.

The Friedel–Crafts reaction between naphthalene and pure *n*-valeryl chloride in nitrobenzene solution gave a good yield of 2-naphthyl-*n*-butyl ketone. Reduction of the carefully purified crystalline ketone led to the pure hydrocarbon.

Experimental.

1-n-*Amylnaphthalene*. *n*-Amyl bromide: A commercial sample of pure *n*-amyl alcohol on distillation gave a main fraction b.p. 137° to 138°, 760 mm, n_D^{20} 1·4099. (Literature, b.p. 138° at 760 mm, n_D^{20} 1·4101.)

To 1050 g of 48-per cent hydrobromic acid in a 3-litre round flask 163 cc of conc sulphuric acid were added with shaking. 440 g of the distilled amyl alcohol were added, followed by 27 cc of conc sulphuric acid. After refluxing for 3 hr the mixture was distilled until the upper layer had disappeared. The halide layer of the distillate was washed with water, sodium carbonate solution, with water, and dried with calcium chloride. It distilled at 129° (literature, 129·7°), and the yield was 495 g (66 per cent).

Sodium (21 g, 0·9 g atom) in thin slices and dry ether (150 cc) were cooled to 0° in a 500-cc reflux apparatus.[9] A mixture of pure 1-bromonaphthalene (60·7 g, 0·29 mole, m.p. 5·9°) and *n*-amyl bromide (50 g, 0·33 mole) was cooled to 0° and added down the condenser during 5 min. The flask was removed from the ice-bath and the reaction started spontaneously after 10 min; during the first ½ hr it was necessary occasionally to cool the flask in ice-water. After 3 hr the reaction subsided and the mixture stood overnight; it then was filtered. The residual sodium bromide and sodium metal were extracted with ether; extract and filtrate were evaporated and the residual oil distilled. It gave a main fraction boiling at 160° to 170° at 19 mm (30·4 g) and this on distillation from sodium gave 26 g (45 per cent yield) of pure 1-*n*-amylnaphthalene, b.p. 164° to 165° at 19 mm, 306° to 307° at 752 mm; m.p. − 26°; n_D^{20} 1·5732. (Found: C, 90·7; H, 9·1 per cent. $C_{15}H_{18}$ requires C, 90·9; H, 9·1 per cent.) 0·43 g of hydrocarbon and 0·477 g of *s*-trinitrobenzene in 15 cc of dry ethyl alcohol gave yellow needles of the *complex*, m.p. 75°. (Found: N, 10·0 per cent. $C_{15}H_{18}{\cdot}C_6H_3O_6N_3$ requires N, 10·2 per cent.)

2-*n*-Amylnaphthalene.

n-*Valeronitrile*. A mixture of potassium cyanide (162 g, 2·5 mole), water (125 cc), alcohol (300 cc), and pure *n*-butyl bromide (302 g, 2 mole, b.p. 102° to 103°, n_D^{20} 1·4394) was heated under reflux for 4 hr. (Longer boiling and mechanical stirring would probably improve the yield.) On cooling, the mixture deposited sodium bromide, which was filtered off and the filtrate distilled, using a column, to remove most of the alcohol. The residue formed two layers, and the upper one yielded 81 g (49 per cent yield) of valeronitrile, b.p. 54° to 55° at 17 mm.

n-*Valeric Acid*. Hydrolysis of the nitrile (80 g) by heating 8 hr under reflux with conc sulphuric acid (120 cc) and water (160 cc) followed by pouring into water (160 cc) and isolating the acid with the aid of ether gave 72 g (73 per cent yield) of *n*-valeric acid, b.p. 103° to 104° at 33 mm.

n-*Valeryl Chloride*. When *n*-valeric acid (72 g, 0·77 mole) was very slowly added from a tap funnel to boiling thionyl chloride (67 cc, 0·95 mole) and the mixture refluxed for 2 hr, the resulting acid chloride distilled at 125° to 130°. On redistillation, through a column, it gave a main fraction (73 g, 86 per cent yield) of b.p. 127° to 128°.

2-*Naphthyl*-n-*Butyl Ketone*. To a solution of naphthalene (64 g, 0·5

mole) and *n*-valeryl chloride (73 g, 0·6 mole) in nitrobenzene (270 cc) at − 5° was added gradually anhydrous aluminium chloride (80 g, 0·6 mole of powder). This yielded 72 g (68 per cent) of 2-naphthyl-*n*-butyl ketone, b.p. 192° to 195° at 16 mm, which solidified on cooling. The ketone crystallized from alcohol in glistening plates, m.p. 54° to 55°, unchanged by recrystallization. Buu-Hoï and Cagniant [6] stated that their preparation of this ketone melted at 34°, but they gave no details of the purity of the valeric acid used. The m.p., 54° to 55°, is only 1° lower than that of 2-naphthyl-*n*-propyl ketone, but a mixture of these two melted at 40° to 41°. [Analysis of ketone m.p. 54° to 55°, found : C, 84·9; H, 7·6 per cent. $C_{15}H_{16}O$ requires C, 84·9; H, 7·55 per cent.] The *semicarbazone* melted at 167° when crude, or when crystallized from alcohol. (Found : C, 71·4; H, 7·2; N, 15·4 per cent. $C_{16}H_{19}ON_3$ requires C, 71·4; H, 7·1; N, 15·6 per cent.) Heating the ketone in aqueous alcohol with excess of hydroxylamine hydrochloride and sodium carbonate for 5 hr gave the *oxime* which, crystallized from alcohol, melted at 87°. (Found : N, 6·4 per cent. $C_{15}H_{17}ON$ requires N, 6·2 per cent.)

2-n-*Amylnaphthalene*. 2-Naphthyl-*n*-butyl ketone (10 g) was reduced by the Huang-Minlon modification [7] of the Wolff–Kishner method, using sodium (2·5 g), diethylene glycol (70 cc), and hydrazine hydrate (5 cc of 85 per cent) and boiling for 4 hr (at 200°). The product (7·6 g) distilled at 163° at 15 mm. Distillation with a column gave a main fraction, b.p. 163° at 15 mm (7·2 g), of n_D^{20} 1·5695, and redistillation gave a colourless oil, b.p. 164° at 15 mm, 310° at 752 mm; m.p. − 4°; n_D^{20} 1·5694. (Found : C, 90·8; H, 9·1 per cent. $C_{15}H_{18}$ requires C, 90·9; H, 9·1 per cent.)

Molecular Complex. On mixing a solution of picric acid in alcohol with one of the hydrocarbon in alcohol there was no deepening of colour and no picrate could be isolated. But equivalent quantities of hydrocarbon and *s*-trinitrobenzene in hot alcohol gave yellow needles of the *complex*, m.p. 74°. (Found : N, 10·4 per cent. $C_{15}H_{18}{\cdot}C_6H_3O_6N_3$ requires N, 10·2 per cent.)

1-*n*-Hexylnaphthalene.

This hydrocarbon was studied before the *n*-butyl and amyl homologues; consequently, several methods of synthesis were explored :—

1. The Friedel–Crafts reaction between *n*-hexoyl chloride and naphthalene in carbon disulphide solution appeared to give little, if any, of the α-ketone.

2. A mixture of α-naphthonitrile and *n*-amylmagnesium bromide, refluxed in ether–benzene solution, gave mainly unchanged starting material. (Compare [9a].)

3. α-Naphthylmagnesium bromide and capronitrile (α-hexonitrile) gave a moderate yield of the desired ketone, but this proved an unreactive substance.

4. By the action of *n*-hexylmagnesium bromide on α-tetralone the carbinol was formed in poor yield. Dehydration of the carbinol followed by dehydrogenation of the olefin gave a mixture from which α-*n*-hexylnaphthalene was isolated.

5. A Wurtz–Fittig reaction between α-bromonaphthalene and *n*-hexyl bromide in ether solution gave a 30 per cent yield of the desired hydrocarbon.

The physical constants of the products obtained by methods 4 and 5 were in close agreement.

Experimental.

1. Friedel–Crafts reaction in carbon disulphide : see p. 116.

2. α-Bromonaphthalene was converted into α-naphthonitrile by heating with cuprous cyanide in pyridine.[10] The yield was 83 per cent of nitrile, m.p. 33°. To an ethereal solution of *n*-amylmagnesium bromide (2 mol), α-naphthonitrile (1 mol) in toluene was added and the mixture refluxed for 22 hr. (Compare the preparation of methyl ketones.[11]) A very small yield of the ketone fraction, b.p. 160° to 180° at 0·8 mm, was obtained.

3. α-*Naphthyl*-n-*Amyl Ketone* from hexonitrile : A mixture of potassium cyanide (23 g, 1·1 mol), water (30 cc), alcohol (75 cc), and *n*-amyl bromide (50 g, 1 mol) refluxed for 5 hr gave 20 g (63 per cent yield) of the nitrile, b.p. 160° to 164°, n_D^{20} 1·4075. Simon [12] gave n_D^{20} 1·4074. To a solution of α-naphthylmagnesium bromide (from α-bromonaphthalene, 56 g, 1·3 mol; magnesium 7 g, 1·4 atm; and ether, 120 cc), benzene (100 cc) was added and most of the ether distilled. Hexonitrile (20 g, 1 mol) in benzene (30 cc) was added and the mixture refluxed for 12 hr. After addition of ice-water, conc hydrochloric acid was added and the mixture refluxed for 3 hr. The organic layer on working up gave 10 g (25 per cent yield) of liquid b.p. 130° at 0·05 mm, free from halogen. This *liquid*, dissolved in acetone–alcohol, and cooled to − 50°, deposited crystals of m.p. − 13° to − 12°, n_D^{20} 1·5806. (Found : C, 84·9; H, 8·2 per cent. $C_{16}H_{18}O$ requires C, 85·0; H, 8·0 per cent.) This substance failed to react with semicarbazide, phenylsemicarbazide, phenylhydrazine, or 2 : 4-dinitrophenylhydrazine. Dr D. H. Whiffen, of the Physical Chemistry Department, kindly examined the infra-red spectrum of this substance and reported that it had a very strong band at 1683 wave-numbers, which is the expected figure for the carbonyl group (acetophenone, 1685 wave-numbers). (Compare [9a].)

4. From *n*-Hexylmagnesium bromide and α-tetralone : A commercial sample of *n*-hexyl alcohol boiled at 154° to 157° and had n_D^{20} 1·4202; it was unsaturated ($KMnO_4$ test). The sample was therefore hydrogenated at 150° and 100 atm in presence of Raney nickel and the product gave a main fraction boiling at 157·5° (corr), n_D^{20} 1·4178. In the literature [13] the values, b.p. 157°, and n_D^{20} 1·4178 are recorded.

Refluxing the alcohol (153 g), 48 per cent hydrobromic acid (315 g) and sulphuric acid (170 g) for 4 hr and working up in the usual way [14] gave the bromide, b.p. 155·5° to 157° at 767 mm. On redistillation a main fraction of b.p. 156·4° to 157·0°, n_D^{20} 1·4477, was obtained. Values in the literature are, b.p. 154° to 156° at 760 mm, n_D^{20} 1·4477.[15]

n-Hexyl bromide (82·5 g, 0·5 mole) and magnesium (12·5 g, 0·52 g atom) reacted vigorously in dry ether (250 cc), but left much unchanged magnesium, even after the mixture had been stirred and refluxed for 1 hr. (This was presumably due to the side reaction : $2RBr + Mg \longrightarrow R{-}R + MgBr_2$.)

To the solution of the Grignard reagent, stirred at − 15° to − 10°, a cold solution of redistilled α-tetralone (48·7 g, 0·33 mol) in dry ether

(100 cc) was slowly added. The mixture was then stirred at room temperature, left overnight, and finally refluxed for 1 hr. When the ether was being removed from the resulting carbinol, water seemed to be lost, and it was decided to isolate the olefin instead of the carbinol. Iodine (0·5 g) was added, the mixture was heated at 100° for 20 min and then slowly distilled; there was a halt at 156° and then at 170°, but much boiled above 250° and water seemed to be produced. The fractions were recombined, mixed with twice their bulk of formic acid (D 1·2) and refluxed for ½ hr. On distillation at 20 mm the recovered product gave (*a*) 18 cc of b.p. 110° to 115° (possibly dodecane, b.p. 215° at 760 mm); (*b*) 11 cc, b.p. 115° to 125°; (*c*) the main fraction, 30 cc of b.p. 156° to 180°, n_D^{20} 1·539; finally a residue of 10 cc. From the main fraction a specimen of hydrocarbon of b.p. 105° to 110° at 0·06 mm was obtained by careful distillation. (Found: C, 89·7; H, 10·2 per cent. $C_{16}H_{22}$ requires C, 89·7; H, 10·3 per cent.)

Dehydrogenation. The olefin (3 g) mixed with palladized charcoal (0·5 g containing 0·1 g Pd) was heated in a metal bath while a slow stream of nitrogen was passed through the liquid. Hydrogen was evolved at 240°, and the temperature was gradually raised during 3 hr to 315°, when evolution of hydrogen almost ceased. The product, isolated with the aid of petroleum-ether, boiled at 125° at 0·05 mm and had n_D^{20} 1·5655. (Found: C, 90·4; H, 9·5 per cent. $C_{16}H_{20}$ requires C, 90·6; H, 9·4 per cent.)

In a second experiment 20 g of the fraction (*c*) (n_D^{20} 1·538, b.p. 156° to 180° at 20 mm, see above) were heated at 240° to 260° for 2 hr with 3 g of 20 per cent palladized charcoal and then for 2 hr at 260° to 300°. The main fraction of the product had n_D^{20} 1·5676 and was unsaturated. Heated with sodium metal up to 260° and then distilled it gave a colourless liquid of n_D^{20} 1·5660. Reheated with palladized charcoal at 300° the liquid gave a small fraction of b.p. 164° to 172° at 10 mm, slightly unsaturated; a main fraction, b.p. 172° to 174° at 10 mm, n_D^{20} 1·5654, saturated; and a residual dark liquid, n_D^{20} 1·5673. (It is possible that one of the impurities is α-hexylidene tetralin which is removable by polymerization with sodium.) When the main fraction was left several hours at − 80° it set to a solid which, on being allowed to warm up, had a steady melting point of − 19° (thermometer in the liquid).

1-n-*Hexylnaphthalene by the Wurtz–Fittig Reaction.* Sodium (41 g, 0·46 equiv) was cut into thin slices and added to sodium-dried ether (150 cc) in a 750-cc flask provided with a reflux condenser. An ice-cold mixture of α-bromonaphthalene (m.p. 5·9° to 6·0°, 62·1 g, 0·3 mole) and pure *n*-hexylbromide (55 g, 0·33 mole) was added and the flask allowed to warm up. Reaction began within 5 min, and when the boiling became too vigorous the flask was cooled in ice-water. After ½ hr the mixture boiled gently and was left going for 2½ hr; it was then kept overnight at room temperature.

The yellow liquid was decanted and filtered, and the residual sodium washed by refluxing with two lots of 50 cc of dry ether. To the united filtrate and washings, sodium wire (9 g) was added and the liquid refluxed for 6 hr: a small amount of sodium bromide formed. After the liquid had been filtered and evaporated the residual oil was free from halogen.

On distillation from a Claisen flask the oil gave a first fraction (12 g of b.p. 100° to 130° at 11 mm) which partly solidified and was probably a mixture of naphthalene and dodecane; a fraction, 34·3 g, of b.p. 130° to 210° at 13 mm (mainly 180° to 185°); and a residue, 10 to 15 g, of fluorescent oil.

Redistillation of the main fraction through a column gave (1) 4·7 g, up to 176° at 13 mm and containing naphthalene; (2) 7·0 g, b.p. 176° at 13 mm, n_D^{20} 1·5657; (3) 20·1 g, b.p. 176° to 180°, n_D^{20} 1·5650. The 27 g of fractions (2) and (3) were fairly pure α-*n*-hexylnaphthalene and represented a yield of 43 per cent, calculated on the α-bromonaphthalene. These fractions were united and refractionated, giving (1) a few drops boiling below 173·5° at 11 mm; (2) 3·8 g of b.p. 173·5° at 11 mm, n_D^{20} 1·5667; (3) 22·5 g of b.p. 173·5° to 173·7° at 11 mm, n_D^{20} 1·5653, and a residue of 0·5 cc. Fraction (3) represents a 35 per cent yield from the original bromonaphthalene. Redistillation of (3) gave 2·5 g of b.p. 177° at 12 mm and n_D^{20} 1·5660; 4·5 g, b.p. 176° at 11 mm, n_D^{20} 1·5653, m.p. − 17·7°; 14·5 g of b.p. 175° at 10 mm, 321° to 322° at 760 mm, n_D^{20} 1·5652, m.p. − 18·2°. (The melting points were taken with the thermometer immersed in the liquid.)

s-*Trinitrobenzene Complex.* To a solution of *s*-trinitrobenzene (0·25 g, 1 mol) in *iso*propyl alcohol (9 cc) was added a solution of the hydrocarbon (0·3 g, 1·2 mol) in *iso*propyl alcohol (2 cc). The colour deepened and yellow crystals formed. These crystals were not homogeneous and melted with decomposition over the range 69° to 74°. (Found : N, 10·6 per cent. $C_{16}H_{20}\cdot C_6H_3O_6N_3$ requires N, 9·9 per cent.)

2-*n*-Hexylnaphthalene.

Again the β-naphthylalkyl ketone was a readily obtainable and well crystallized substance. It was made by the Friedel–Crafts reaction, using either carbon disulphide or nitrobenzene as solvent. As the commercial caproic acid appeared to be very impure, *n*-hexoic acid was synthesized from crotonaldehyde *via* the high-melting sorbic acid,

$$CH_3—CH=CH—CH=CH—COOH.$$

In contrast to α-naphthyl-*n*-amyl ketone the β-isomer had a reactive carbonyl group, readily forming the usual derivatives. Oxidation of the side-chain was difficult, but reaction with selenium dioxide followed by hydrogen peroxide yielded β-naphthoic acid, proving the β-position of the side-chain. Reduction by either the Clemmensen or the Wolff–Kishner method gave the hydrocarbon. From this hydrocarbon neither the picrate nor the styphnate could be obtained; the complex with *s*-trinitrobenzene was always contaminated with the nitro-compound.

Experimental.

n-*Hexoic Acid.* A commercial sample of "pure caproic acid" was found to melt below − 10° and, on distillation through a column, gave fractions boiling between 195° and 205°; the m.p. varied from − 15° to − 8°. *n*-Hexoic acid boils at 208° (corr) and freezes at − 3·5°.[16] The pure acid was therefore synthesized *via* sorbic acid. Following the directions of Doebner,[17] crotonaldehyde (80 g, 1·00 mol), malonic acid

(120 g, 1·01 mol), and dry pyridine (120 g, 1·33 mol) were heated on a water-bath for 3 hr. The liquid was cooled in ice, and the sorbic acid, precipitated by the addition of 20 per cent sulphuric acid, was washed with a little water and then recrystallized from hot water. Several experiments gave an average yield of 27 g (21 per cent of the theoretical) of crystals melting at 130° to 132°. Doebner [17] claims a 31 per cent yield of acid melting at 134°. Sorbic acid (56 g, m.p. 130° to 132°) dissolved in dioxan (200 cc) was hydrogenated at room temperature with hydrogen (at 50 atm) in presence of Raney nickel, the temperature finally being raised to 60°. The yield was 51 g (90 per cent) of acid, m.p. — 3°, stable to dilute permanganate after standing for several hours. On distillation the acid gave a main fraction, b.p. 203° to 204° (uncorr), m.p. — 3°.

n-Hexoyl Chloride. *n*-Hexoic acid (50 g, m.p. — 3°, 1 mol) and thionyl chloride (62 g, 1·2 mol) were allowed to react and the mixture then heated for 90 min under reflux. Distillation gave 50 g (86 per cent yield) of the *n*-hexoyl chloride, b.p. 149° to 153°.

2-Naphthyl-n-Amyl Ketone. To a solution of naphthalene (32 g, 1·1 mol) and *n*-hexoyl chloride (30 g, 1 mol) in redistilled nitrobenzene (160 g) stirred and cooled to — 5° was added powdered aluminium chloride (30 g, 1 mol) in small quantities during an hour, the temperature not exceeding 0°.

After having stood 20 min the reaction mixture was poured on to ice. From the nitrobenzene layer a crude ketone fraction of b.p. 180° to 190° at 4 mm was obtained; this solidified and then melted at 63·5° to 66·5°. The yield was 25 g (48 per cent, calculated on acid chloride); in a second experiment, in which the cold reaction-mixture was stirred for a longer time (1 hr) after the end of the addition, the yield dropped to 44 per cent.

When the ketone had been crystallized from *n*-propyl alcohol it melted at 67·5° to 68·5°, unchanged by further crystallization from acetic acid, ethyl alcohol, or light petroleum. (Found: C, 84·6; H, 8·0 per cent. Calc. for $C_{16}H_{18}O$ C, 85·0; H, 7·9 per cent.) Buu-Hoï and Cagniant [6] give m.p. 68°. The *semicarbazone*, prepared readily in aqueous-alcoholic solution, and crystallized from alcohol, melted at 153° to 154°. (Found: N, 15·2 per cent. $C_{17}H_{21}ON_3$ requires N, 14·8 per cent.) The scarlet 2 : 4-*dinitrophenylhydrazone*, crystallized from *n*-propyl alcohol, melted at 200° to 201°. (Found: C, 64·9; H, 5·4; N, 14·1 per cent. $C_{22}H_{22}O_4N_4$ requires C, 65·0; H, 5·4; N, 13·8 per cent.)

Oxidation of the Ketone. Heating the ketone (1 g) with nitric acid (5 cc) and water (10 cc) for 24 hr to 160° gave a product of m.p. 185° to 215° which contained nitrogen and could not be purified. Use of more dilute nitric acid gave a similar product; sodium-hypochlorite solution left the ketone almost unattacked.

The ketone (3·0 g) in dioxan (25 cc) was heated under reflux with sublimed selenium dioxide (2 g) for 3 hr; a further 1 g of selenium dioxide was added, the mixture heated again for 5 hr, and allowed to stand overnight. The liquid was decanted from the selenium, poured into water in a separating funnel, and the oxidation product, a red oil presumably a 1 : 2-diketone, isolated with the aid of ether. This oil was not purified but was suspended in 30 per cent hydrogen peroxide (30 cc) and to the mixture a solution of sodium hydroxide (5 g) in water (25 cc) was added slowly; after standing for 1 hr the mixture was extracted with ether to

remove neutral products and then was acidified. The pale yellow solid (1·0 g, 44 per cent yield) was crystallized three times from toluene–ligroin mixture and yielded colourless crystals of m.p. 183° to 184°, which is the recorded m.p. of β-naphthoic acid. (Found : C, 77·0; H, 4·7 per cent; equivalent, 170. Calc for $C_{11}H_8O_2$ C, 76·8; H, 4·6 per cent; equivalent 172.) This acid yielded an amide of m.p. 192° to 193°. (Literature, m.p. 192° and 195°.)

Friedel–Crafts Reaction in Carbon Disulphide. Naphthalene (32 g, 1·1 mol) and *n*-hexoyl chloride (30 g, 1 mol) were dissolved in carbon disulphide (150 g), and powdered aluminium chloride (30 g) slowly added at 20°. The mixture was stirred for 6 hr and then left overnight. On working up in the usual way 27 g (51 per cent yield, calculated on the acid chloride) of a crude ketone fraction, b.p. 150° to 180° at 0·4 mm, was obtained. Crystallized from *n*-propyl alcohol the product yielded 22 g of crystals in three crops, all melting between 66·5° and 68°. As the m.p. of the β-ketone is 67·5° to 68·5° and of the α-ketone is — 13°, there is either very little α-ketone formed by the Friedel–Crafts reaction even in carbon-disulphide solution, or the α-ketone which is produced is destroyed later by the aluminium chloride.

β-n-*Hexylnaphthalene.* Reduction of the ketone by the Clemmensen method gave 65 per cent yields of hydrocarbon, b.p. 145° to 150° at 4 mm, n_D^{20} 1·5645. The Wolff–Kishner method (heating the semicarbazone with sodium ethoxide in alcohol at 200° for 27 hr) gave a 78 per cent yield of colourless liquid, b.p. 126° to 134° at 0·1 mm, n_D^{20} 1·5622. When this liquid was crystallized from acetone at — 60° it melted at — 6·0° to — 5·8°; recrystallization from acetone gave a product of b.p. 136° to 138° at 2 mm, m.p. — 5·6°, n_D^{20} 1·5620. (Found : C, 90·6; H, 9·5 per cent. ($C_{16}H_{20}$ requires C, 90·6; H, 9·4 per cent.)

As the hydrocarbon obtained by the Clemmensen reduction was slightly yellow it was heated with sodium (1 g metal to 9 g of hydrocarbon) at 200° for ½ hr, the dark liquid then decanted and distilled. The main fraction boiled at 110° to 115° at 0·02 mm and had n_D^{20} 1·5629. Crystallization from acetone gave a colourless solid of m.p. — 6·2° to — 5·8°, b.p. 322° to 323° at 760 mm, 136° to 138° at 2 mm, and n_D^{20} 1·5622.

s-*Trinitrobenzene Complex.* To a solution of *s*-trinitrobenzene (0·4 g, 1 mol) in *iso*propyl alcohol (8 cc) a solution of the hydrocarbon (0·5 g, 1·25 mol) in *iso*propyl alcohol (2 cc) was added. Sulphur-yellow crystals separated, but these melted at 67° to 69° leaving a residue, solid at 74°. (Found : N, 12·0 per cent. Calc N, 9·9 per cent.)

ACKNOWLEDGMENTS.

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EVAPORATION PROCESSES IN A BURNING KEROSINE SPRAY.

By H. G. Wolfhard and W. G. Parker.*

Summary.

Consideration has been given to the evaporation of kerosine droplets in a fine spray burning in still air at room temperature. A theoretical discussion of the heat available for evaporation has shown that in the conditions examined no significant evaporation of the droplets occurs before the preheating zone of the flame. This zone is very narrow, but there is sufficient time for the smallest droplets to vaporize and diffuse into the gases in this zone. Thus an inflammable mixture is formed which maintains the flame front. Some experimental evidence in support of this argument was obtained in photographs of kerosine droplets entering the preheating zone of a non-aerated Bunsen-type gas flame.

Introduction.

When a fine spray of kerosine is projected horizontally from a suitable nozzle and ignited in still air a stationary flame is obtained at a certain critical distance from the nozzle. Apart from the complex chemical processes associated with the phenomenon of combustion there are some important physical processes taking place. The most vital question on these is how the flame front is maintained and where the liquid droplets are converted into vapour. Schlieren photography has not proved helpful in showing any line of demarcation between the liquid and vapour phases, probably on account of the presence of strong "temperature" Schliere in the same region, and a theoretical analysis of conditions is necessary. An analysis of this kind was undertaken based on the physical dimensions of the spray. Consideration was first given to the free evaporation of fuel droplets in the space between the nozzle and the flame front. From this it was clear that at room temperature an adequate vapour concentration for combustion could not be reached even allowing for the radiation effect of the flame, and it was necessary therefore to estimate the heat transfer to the droplets in the steep temperature gradient immediately in front of the flame. This pre-heating zone, which is always clearly observed in Schlieren light, is relatively narrow. Nevertheless, it was found that the smallest droplets have ample time to vaporize and diffuse into the gases in this zone, and thus provide an inflammable mixture which maintains the flame front. This theoretical argument has received support experimentally from photographs of kerosine droplets entering the preheating zone of a pre-mixed gas flame.

Description of Spray and Method of Analysis.

The spray examined was obtained from a very fine nozzle (0·25 mm diameter) which was fixed horizontally about 4 ft above the ground in still air. Ordinary domestic kerosine was fed to the nozzle from a pressurized container. On ignition, the spray burned as a stationary luminous

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flame beginning a few cm from the nozzle. A characteristic Schlieren photograph of this spray is shown in Fig. 1. The nozzle is just visible on the left, and behind it is the circular field of the Schlieren head. The Schlieren from the burning spray begins near the centre of this field, and is partially obscured on the right by direct light from the spray, which grows more intense some distance beyond the flame front. The shape of the flame is remarkable, since it is similar to an inverted cone of a Bunsen burner. This shape is characteristic of more or less pre-mixed gases.

From a simple measurement of the volumetric flow of kerosine (2 cc/sec) and the diameter of the orifice (0·025 cm) it was found that the average forward velocity component of the liquid stream leaving the nozzle was 41 m/sec. This stream breaks up into droplets of widely varying diameters. Let us consider two different sizes, viz., 0·01 cm diameter (big droplets) and 0·001 cm diameter (small droplets), and calculate the resistance which such droplets experience as they travel through the air.

The average Reynolds Number for the small droplets, calculated in the usual way, is initially approximately 14. Stoke's Law of friction holds for Reynolds Number up to 1, and above 1 the actual friction is greater than the calculated value, but the deviation is still very small. This justifies use of the relationship :—

$$W = 6\pi\eta r v$$

where
η = viscosity (g/cm/sec)
r = radius of droplet
v = velocity of droplet

to calculate the frictional force W on the small droplets. For the big droplets Stoke's Law can only be applied if it is assumed that the velocity falls off in a short distance and that velocities of about 4 m/sec and less are within the scope of Stoke's Law. This has been done and has clearly given what is more or less a lower limit for the frictional force.

The distance x which a droplet travels in time t can now be calculated from the equation

$$m\frac{d^2x}{dt^2} + K\frac{dx}{dt} = 0$$

where
m = mass of droplet
and
K = coefficient of friction
$= 6\pi\eta r$

The general solution of this equation is

$$x = A + Be^{-\frac{K}{m}t}$$

if for $t = 0$, $x = 0$, then $A = -B$
and by differentiating we obtain

$$\frac{dx}{dt} = -B\frac{K}{m}e^{-\frac{K}{m}t}$$

when $t = 0$, $\frac{dx}{dt} = U_0$, where U_0 is the initial velocity (41 m/sec in this case) and $B = \frac{-mU_0}{K}$.

Hence $$x = \frac{U_0 m}{K} - \frac{U_0 m}{K} e^{-\frac{K}{m}t}.$$

If t is made large, then the second expression on the right disappears and it is seen that droplets shot into stationary air have a definite range which they cannot exceed. This range $\left(= \frac{U_0 m}{K}\right)$ is proportional to the square of the diameter of the droplet and the initial velocity.

The mass of the small droplets (sp. gr. 0·8) is $4{\cdot}2 \times 10^{-10}$ g and of the large droplets $4{\cdot}2 \times 10^{-7}$ g, while the frictional coefficients are $1{\cdot}7 \times 10^{-6}$ and $1{\cdot}7 \times 10^{-5}$ respectively. From this, the range of the small droplets is *ca* 1 cm and for the big droplets not more than 100 cm (an upper limit).

Shortly after their formation, therefore, the droplets have widely different velocities, and the bigger droplets may collide with and absorb some of the small droplets so that the proportion of these may be different in different parts of the spray.

Velocity of Entrained Air.

If the frictional effect of the air on the droplets is treated as inelastic collisions then as soon as the droplets have no velocity relative to the air (except a sedimentation velocity), the air and the droplets must have the momentum of the original spray. This means that the air in the spray commences to move and behave as an independent jet. The forward momentum/sec of the kerosine spray in question which delivered 2 cc/sec with an initial forward velocity of 41 m/sec, was

$$65{\cdot}6 \times 10^2 \text{ (g cm/sec}^2\text{)} \quad . \quad . \quad . \quad . \quad (1)$$

The largest droplets actually observed in the spray were about 0·008 cm diameter with a corresponding maximum range of about 64 cm. So it may be assumed that after 50 cm a substantial part of the droplets have come to rest relative to air. At this point the spray covered an area of about 400 cm^2. The mass flow of air with mean velocity v, passing through that area was therefore

$$400 \times v \times 1{\cdot}3 \times 10^{-3}$$

and the momentum of the air and droplets was therefore

$$(400 \times v \times 1{\cdot}3 \times 10^{-3} + 2 \times 0{\cdot}8)v \quad . \quad . \quad . \quad . \quad (2)$$

Equating (1) and (2) and solving

$$v \simeq 111 \text{ cm/sec.}$$

Beyond this point the velocity of the mixed jet of air and droplets decreased because the diameter was increasing.

From the shape of the spray, which was parabolic at first, it seemed that the air velocity was small initially, increased subsequently, and became fairly constant at about 1 m/sec up to the point where all the droplets had come to rest in the air.

Evaporation of Droplets in Free Space.

In our burner the distance of the flame front from the nozzle (see Fig. 1) is about 2·5 cm. From the above discussion it is concluded that the

smallest droplets have already come to rest in the air and move with the air velocity which may be 20 to 30 cm/sec at this point. This is compatible with known flame velocities, and the flame front therefore remains stationary against the jet velocity. The time from the nozzle to the flame front must be less than 0·1 sec for the smallest droplets and very much less than this for larger droplets. It is important to decide therefore whether the smaller droplets are able to evaporate in this time and whether a sufficient number can evaporate freely in the air to form an inflammable gas mixture. The answer is definitely negative, since it is possible to carry very small droplets over big distances and still observe them as liquid. The fuel-vapour concentration cannot exceed the saturation value corresponding to the air temperature and since the flash point of kerosine (*i.e.*, the lower limit of inflammability) is 20° C or more above room temperature, it is impossible to get an equilibrium mixture of fuel vapour and air which is inflammable. Moreover, if the evaporation of the single droplet in an unlimited amount of air (where equilibrium conditions do not apply) is considered it is found to be negligible after 0·1 sec. Niels Frössling has calculated the rate of decrease in diameter of droplets of various substances. Water droplets of 10 μ diameter, which have a much higher vapour pressure than kerosine, decrease about 10 per cent in diameter in 0·1 sec, while naphthalene, which is more nearly comparable with kerosine, is found to decrease by only 1 per cent in the same time. The increase of vapour pressure corresponding to the increased surface tension as the droplets get smaller, is not a significant effect either, since a decrease in radius from 10^{-3} to 10^{-5} cm is accompanied by an increase of vapour pressure of less than 1 per cent.

Effect of Radiation from the Flame.

Consideration must also be given to radiation effects from the flame. Absorption of radiant energy by the droplets is rather a complex problem. Hydrocarbons are nearly transparent to all wavelengths up to 6 μ with the exception of the CH band at 3·5 μ. At wavelengths greater than 6 μ there is fairly heavy absorption. Air, on the other hand, is transparent to all radiations in question. Since it is necessary, however, for the air temperature to rise in order that any increase in vapour pressure of droplets absorbing radiant energy can be effective, this must be brought about by heat transfer from the droplets themselves. A droplet does not get its radiation from the flame front, but from a part of the flame where intense black-body radiations are emitted by hot carbon particles. This part is somewhat beyond the flame front (as shown by the direct light in Fig. 1) and subtends a rather small angle with a droplet approaching the flame front. If it is assumed that the temperature of the radiating part of the flame is 1500° C, then from Wien's Displacement Law the wavelength for maximum energy emitted is given by

$$\lambda_{max.} T = 0{\cdot}288$$

or

$$\lambda_{max.} = 1{\cdot}6\ \mu.$$

Between $\lambda = 0 - 6\ \mu$, therefore, about 93 per cent of the total radiation for 1500° C occurs and only 7 per cent remains in the region where stronger

absorption takes place. This figure, viz., 7 per cent, is almost certainly too high, since the droplet diameter of 0·001 cm is an extremely thin layer for total absorption, and the true figure for the droplets of this size is probably under 5 per cent, including absorption by the CH band at 3·5 μ.

The solid angle subtended at the droplet by the radiating part of the flame is very roughly 1/20 of the half-space angle (2 π), while the emission coefficient of the flame may be perhaps of the order of 1/10. This latter value is assessed on the fact that the emission coefficient of big industrial furnaces does not reach unity, and the thickness of the optical layer in the flame of our spray is comparatively small.

On these assumptions an upper limit can be estimated for the energy which radiation can actually contribute to a droplet. The radiation absorbed by the droplet is given by

$$Q = ASe\phi a\left(\frac{T}{100}\right)^4 \cdot t$$

where Q = heat received by one droplet
A = area of a droplet (if diameter is 10 μ, $A = 75 \times 10^{-12}\text{m}^2$)
S = radiation from a black body
$= 4{\cdot}96$ k.cal/m²/h/°K⁴
e = emission coefficient of flame (assumed = 0·1)
ϕ = solid angle of effective radiation = 0·05
a = absorption factor for the droplet (assumed to be 5 per cent of total radiation received)
t = time in hours (taken as 0·1 sec)

Substituting the values indicated

$$Q = 2{\cdot}5 \times 10^{-10} \text{ cal/droplet.}$$

The heat required to vaporize the droplet, however, is approximately 600×10^{-10} cal/droplet. Half of this heat is necessary to supply the latent heat of evaporation, and half is required to raise the temperature of the droplet. Complete evaporation of the droplets is impossible, however, since re-condensation must occur (probably as very fine droplets) if the air temperature remains low. In short, therefore, even assuming the above figures be several factors out, it is concluded that no sensible increase in vapour pressure is brought about by radiation before the big and small droplets together with the air meet the flame front. This is true at least in the special case here considered.

Physical Conditions in the Flame Front.

Since there appears to be no significant physical chemical change in the system up to the flame, the conditions in the flame front require careful examination. In general, a flame of any pre-mixed gases consists of an inner cone (or reaction zone), then a region of interconal gas (an equilibrium mixture), and finally an outer cone where CO and other dissociated products are finally oxidized. The Schlieren photograph shows that this flame, too, has an inner cone. Such a cone consists of two parts : (1) a pre-heating zone which gives rise to the Schlieren which we observe in Fig. 1, and (2) a luminous zone (which is not seen in the instantaneous photograph

of Fig. 1) where the reaction takes place.[1] The temperature increase in the preheating zone is from room temperature up to about 800° to 1000° C, and the thickness, which has been measured from the separation of the Schlieren and luminous zone in photographs of bunsen flames, is inversely proportional to the normal flame velocity (V_n).[2] For acetylene the thickness of the zone was found to be 0·24 mm. The normal flame velocity of an acetylene–air flame is between 1·5 and 2·0 m/sec, whereas the flame velocity of kerosine if burnt under pre-mixed conditions is estimated at about 0·2 m/sec. The preheating zone of the kerosine flame is therefore greater and about 2·1 mm.

Heat Transfer in the Preheating Zone.

The heat transfer number α is known for cylindrical-shaped bodies, and we will transpose this to spherical droplets by making the assumption that the heat transfer to a sphere is related to that of a cylinder in the same way as the resistance coefficients (c) are related.

Thus

$$\alpha_{\text{sphere}} = \alpha_{\text{cyl.}} \times \frac{\pi}{4} \frac{C \text{ sphere}}{C \text{ cyl}}$$

and according to Gumz [3]

$$\frac{C \text{ sphere}}{C \text{ cyl}} = 2{\cdot}64\ (Re)^{-0{\cdot}255}$$

where Re the Reynolds No. lies between 0·1 and 100.

The Reynolds No. of the smaller droplet is uncertain and may be a little smaller than 0·1, since the droplet is approximately at rest in the moving air stream and has only its sedimentation velocity. If the Reynolds Number is more nearly 0·01 (*i.e.*, a velocity of about 1 cm/sec) which is likely, since the droplet experiences turbulent air currents as well as a sedimentation force, the error introduced is small because Gumz's value is only dependent on a low power of Re.

For a cylinder with $Re = 0{\cdot}01$, the Nusselt Number $Nu \left(= \frac{\alpha \cdot d}{k}\right)$ is about 0·1.

Hence

$$\alpha_{\text{sphere}} = 0{\cdot}01 \times \frac{\pi}{4} \times 2{\cdot}64 \times (0{\cdot}01)^{-0{\cdot}235}$$

$$\simeq 0{\cdot}007 \text{ (cal/cm}^2\text{/sec/°C)}$$

because

$$Nu = 0{\cdot}1 = \frac{\alpha_{cyl} \cdot d}{k} = \frac{\alpha \cdot 10^{-3}}{10^{-4}}$$

$$\alpha_{cyl} = 10^{-2}$$

where d = diameter

k = mean heat conductivity number between room temperature and 1000° C.

The heat which the droplet (velocity about 20 cm/sec) absorbs in passing

through a preheating zone 2·1 mm thick can now be calculated from the equation :—

$$Q = \alpha.A.(\theta_1 - \theta_2)t$$

where A = surface area of droplet
$= 314 \times 10^{-8}$ cm^2
$\theta_1 - \theta_2$ = average temperature difference
$= 500°$
t = time $= \frac{0{\cdot}21}{20} = 10^{-2}$ sec

$$Q = 0{\cdot}007 \times 314 \times 10^{-8} \times 500 \times 10^{-2}$$
$$= 1{\cdot}1 \times 10^{-7} \text{ cal.}$$

The heat required to evaporate a droplet is of the order $0{\cdot}5 \times 10^{-7}$ (see above), so that there appears to be sufficient heat available to vaporize the smallest droplets in the preheating zone. The calculation is, of course, very rough and neglects, for example, the decrease in diameter of the droplet during evaporation, but it is sufficient to show that the process is feasible.

An explanation is required, however, of the mechanism by which the flame front remains stationary and establishes a heat current towards the unburnt spray, since it seems that this current is the source of heat which vaporizes the smallest droplets.

Assuming that 1 g of fuel is required to burn 7·5 g of air then $1{\cdot}7 \times 10^{-4}$ g of fuel is required for 1 cc of air. One small droplet (10 μ diameter) weighs $0{\cdot}4 \times 10^{-9}$, and hence $\frac{1{\cdot}7 \times 10^{-4}}{0{\cdot}4 \times 10^{-9}} = 4{\cdot}2 \times 10^5$ droplets consume 1 cc of air. Alternatively, one droplet consumes a cube of air with a side of 0·014 cm and when the droplet vaporizes, the vapour must spread about 0·007 cm in each direction so as to feed the flame uniformly. The time to do this can be estimated from the Einstein equation

$$\bar{x}^2 = 2\,Dt$$

where $\bar{x}$ = the average diffusion path
D = diffusion coefficient
t = time.

The value of D is nearly 1 for conditions in a flame.

$$\therefore \quad t = \frac{x^2}{2D} = \frac{0{\cdot}0007^2}{2} = 2{\cdot}5 \times 10^{-5} \text{ sec.}$$

This time is well inside the time which a droplet (or its remainder) takes in passing through the flame front.

The foregoing assessments, therefore, suggest that a smooth flame front can be fed by very small droplets which vaporize directly in its preheating zone.

An attempt was made to test experimentally the validity of the foregoing argument. The apparatus consisted of a kerosine spray (as used in Fig. 1) enclosed in a cylindrical vessel. Air entered the vessel at a point behind the spray nozzle and left again through a $\frac{1}{2}$-in diameter vertical pipe from a point about 8 inches downstream of the spray. Droplets of kerosine were picked up by this air stream and carried to the mouth of the vertical

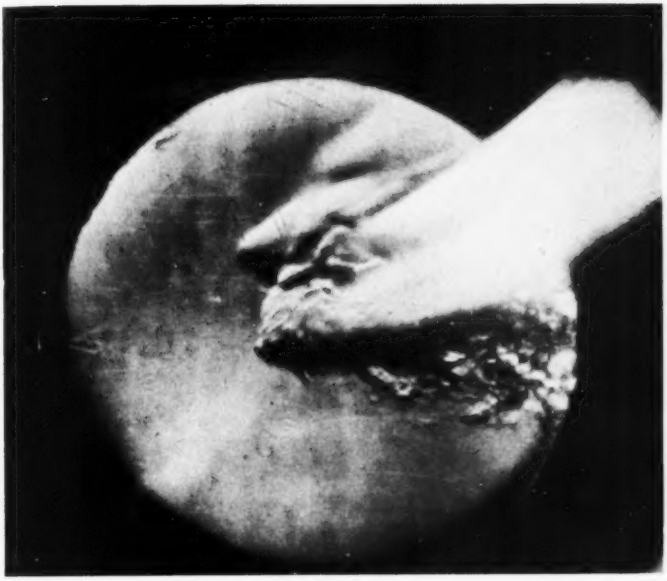

FIG. 1.

SCHLIEREN PHOTOGRAPH OF A KEROSINE SPRAY BURNING IN STILL AIR.

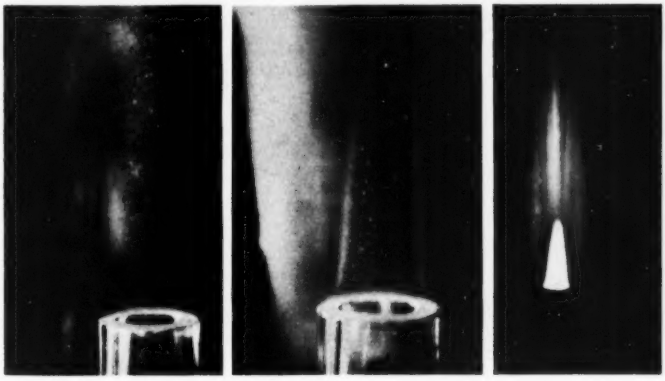

FIG. 2 (*left*).

DROPLETS LEAVING BURNER MOUTH (NO FLAME PRESENT).

FIG. 3 (*centre*).

DROPLETS IN A BUTANE FLAME (REFLECTED LIGHT).

FIG. 4 (*right*).

DIRECT PHOTOGRAPH OF DROPLETS ENTERING AN ACETYLENE–AIR FLAME.

[*To face p.* 124.

FIG. 5.

SCHLIEREN CONE OF AN ACETYLENE–AIR FLAME.

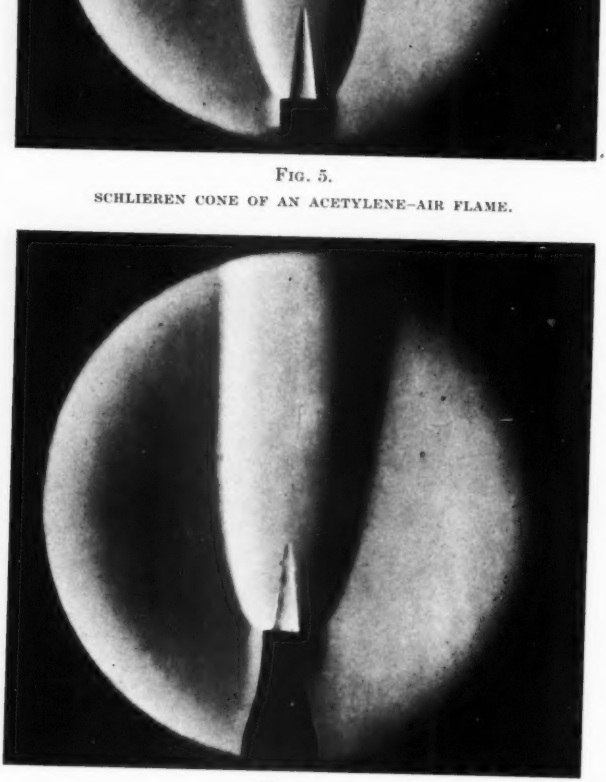

FIG. 6.

SCHLIEREN CONE OF AN ACETYLENE–AIR FLAME SHOWING DEFORMATION BY KEROSINE DROPLET.

pipe. A combustible gas was also fed into the pipe and mixed with the air. The pre-mixed gas could be burnt as a Bunsen flame at the jet (*i.e.*, the mouth of the pipe), and the kerosine droplets were carried up into this flame. We photographed events immediately above the jet in strong light from a discharge lamp.

Fig. 2 shows droplets carried by the gas stream leaving the jet. No flame was present at that time, and patches of light on the left-hand side are caused by reflections on the cylindrical glass walls of the discharge tube. The smallest droplets, which are in much the greater abundance on account of the method of pick-up, were approximately 0·0009 cm diameter and were therefore similar in size to the "small" droplets assumed for our calculations. The bigger droplets seen in the photograph are rather less than 0·003 cm diameter.

Fig. 3 shows the droplets in a butane flame. It is apparent that the droplets do not pass the flame front. A pre-mixed butane flame of this kind does not radiate appreciably because there is no free-carbon formation. The droplets must have evaporated in the preheating zone of the flame.

Conditions could be varied so that a few very large droplets (diameter approximately 0·008 cm) were carried into the flame. Evaporation of these droplets took much longer and was observed to be complete at distances of a few mm above the cone. In that part of the flame there was no oxygen to burn the vapour and the heated vapour began to radiate. Fig. 4, which is a direct photograph of a flame in such conditions, contains a few streaks of light starting above the inner cone, and these are due to large droplets behaving in the manner described. We attempted to get Schlieren photographs of the vapour trails from these droplets after they passed the flame front but were unsuccessful.

Fig. 5 shows the Schlieren cone of an ordinary C_2H_2–air flame, and Fig. 6 shows a deformed cone of this flame which is believed to be due to a large droplet passing through the Schlieren cone at the instant the photograph was taken.

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SOME EXPERIMENTS ON A BEARING AND WEAR-TESTING MACHINE.

By A. Cameron.*

Introduction.

The Engineering Laboratory at Cambridge was presented with a Timken wear and lubricant testing machine by the Chairman of British Timken Ltd., Mr M. B. U. Dewar. It was thought that, although this machine is generally used for testing the film strength of lubricants, it would be more valuable for the department's purpose if it were modified so as to illustrate the principles of film lubrication. It would thus be used as a practical adjunct to the theoretical lectures on lubrication.

After a term's use with the simple modification described below, it was seen that the tester could be used for problems other than teaching, such as testing of the running qualities of bearing metals. With this in view, the experience gained with it is summarized in this note.

Modification of Design.

The Timken tester consists essentially, in its unmodified form, of a disc or " cup " approximately 2 in diameter (the accurate diameter is $6/\pi$ in) and $\frac{1}{2}$ in wide. This is rotated by a 2-h.p. motor via a pulley-and-belt system giving 400, 600, or 850 r.p.m. Against this rotating " cup " a steel block can be pressed by means of a lever-and-weight system, and the frictional drag on the block can be measured. The " cup " and block can both be renewed when worn. There is also a circulating oil-pump and oil-reservoir, which latter rests on an electric hot-plate.

The block is supported on a knife-edge pivot, which is part of the friction-measuring mechanism. The modification, suggested by Dr D. G. Christopherson, was to replace the block by a bronze-fitted partial bearing such that the " cup " worked against a finite area instead of having line contact with the block. The bronze pad was so designed that it had an internal radius equal to the radius of the " cup." The pad was dimensioned so that the knife-edge support was 0·6 of the bearing arc from the leading edge. The pad can therefore be considered as a Michell tilting bearing; its length (in the direction of sliding) was 0·6 in. The leading edge was rounded and given a radius to ensure the smooth formation of the oil film. No other modification was incorporated in the machine.

Test Procedure.

The main object of the experiments was to demonstrate the action of a bearing under conditions of mixed lubrication. The loading- and friction-measuring arrangements are not suitable for investigation of the

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full fluid region, and furthermore, the mixed lubrication region, where part of the load is carried by the oil film and part by metal–metal contact, is very important practically. The particular points to be studied were the way the friction rose with increasing load and how, under suitable conditions, the bearing can be made to " run-in " with a resulting drop in friction with time.

The oil used was a medium machine oil with a viscosity of 240 cs at 20° C and 34 cs at 60° C.

The first run was at 400 r.p.m. at an oil temperature of 30° C. The motor was started at no load, and the loading on the bearing was progressively increased. Friction readings were taken at 2-lb intervals on the loading arm between 0 and 10 lb and then at 5-lb increments to 40 lb.

At 40-lb load on the loading arm, a running-in curve was taken. The loading arm has approximately a tenfold leverage ratio, but varies slightly with the friction. This running-in test consisted of measuring the friction for 15 min or until the friction–time curve flattened out. After this had been done, extra loading weights were added, in 10-lb increments, till the frictional drag increased rapidly to seizure when the motor was stopped, after taking off the load.

The same procedure was adopted at 600 and 800 r.p.m., although the running-in test was omitted.

Application of Theory.

Instead of plotting the coefficient of friction, μ, and frictional drag, F, against the normal variable $\sqrt{\eta U/W}$ (viscosity η, sliding speed U, load per unit width of pad W) they were plotted against the film thickness at the outlet edge, which was calculated from the normal hydrodynamic theory. The relations between (1) the calculated film thickness at the trailing edge h_0 and (2) the theoretical coefficient of fluid friction and the variable $\eta U/W$ are (cp. Boswall, ref. [1]) :—

$$h_0 = \text{L.C.}\left(\frac{\eta U}{W}\right)^{\frac{1}{2}}$$

$$\mu = H\left(\frac{\eta U}{W}\right)^{\frac{1}{2}}$$

so

$$\frac{h_0}{L} = \frac{C}{H}\mu$$

where h_0 = calculated oil-film thickness at outlet
η = viscosity
U = sliding velocity
W = load per unit width
L = length of bearing (in direction of motion)
C and H are constants for the bearing in consistent units

For this bearing $L = 0{\cdot}6$ in, width $= 0{\cdot}5$ in

so $C = 0{\cdot}263$ and $H = 2{\cdot}76$.

As in all this type of work the true viscosity of the oil is uncertain, due to the frictional heating. For purposes of calculation, it was taken as

the viscosity of the oil at the temperature of the reservoir. This is clearly unsatisfactory and the true viscosity must be much lower than that of the bulk oil, but lacking a better assumption this figure will be used.

The reason for plotting h_0 instead of $(\eta U/W)^{\frac{1}{2}}$ (apart from the academic one of working out the film thickness) was to show the order of film thickness at which seizure occurred. The original plan was to measure the surface roughness of the test pieces and compare them with the calculated figures. This was not possible as the surface-finish measuring apparatus was not available, but this will be done in future.

Results.

Typical results are shown in Figs. 1 and 2. The observed frictional drag is first plotted, and then the values of the coefficient of friction calculated from it. The frictional drag increases quite steadily till seizure occurs at a calculated outlet film thickness of 120 micro-inches. This value is

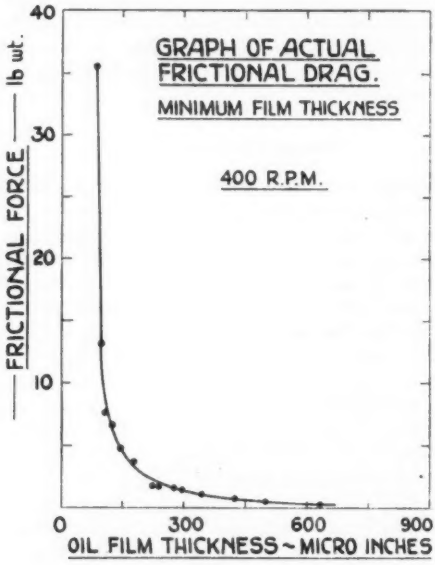

Fig. 1.

higher than would be expected, a fact probably accounted for by the true viscosity being lower than the bulk figure used in the calculation.

The curve for μ against h_0, the outlet film thickness, is unusual and will be commented on further in the discussion.

The curve for running-in is plotted in Fig. 3. The step-wise shape shown here was at first discounted, but its repeated appearance, and the fact that the size of the steps is greater than the experimental scatter, tended to show that it was a genuine effect. Furthermore, a recent

Russian paper [2] quotes experiments where a step-shaped curve results when wear is plotted against time. This author gives a very tentative theoretical explanation of the wear results.

It is interesting to see that full fluid conditions have apparently been

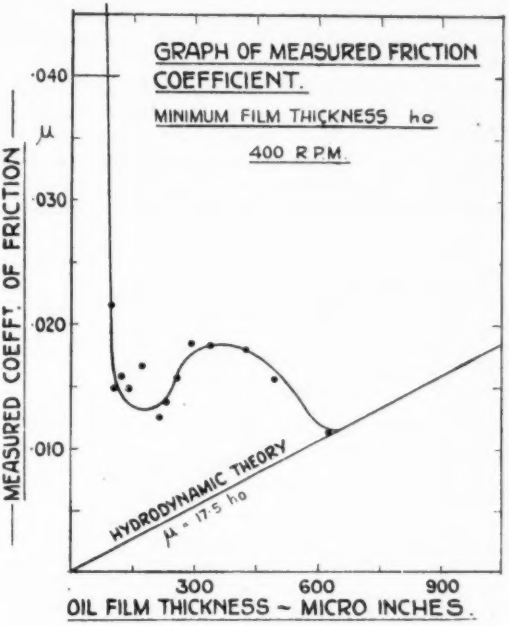

FIG. 2.

achieved at the end of the 15 min running-in. The final frictional drag was too small to measure.

The question of surface finish of the test pieces will be investigated in future work as it is clearly important.

A study of the wear marks on the bronze block showed whether contact along the full width of the cup had been established or not. This was usually satisfactory as the block is mounted on self-aligning supports.

DISCUSSION OF RESULTS.

The frictional-drag–film-thickness curve is plotted in Fig. 1. The drag increases with decreasing film thickness till the system seizes.

The value of the film thickness at seizure is a measure of the running qualities of the material. This quality is very mysterious, and a large number of factors must influence it. It had been hoped to study the roughness of the surface after running, that is the "worn roughness" after wear had taken place, but this could not be done. The interesting

point which needs investigation is how the roughness of the surface as it comes from the finishing operation affects the worn roughness. This relation must be important, as the smoother the surface the greater the load carried hydrodynamically. Thus a thinner film can be tolerated without metal contact occurring, and hence a larger load can be supported.

In Fig. 2 the coefficient of friction is plotted against h_0. The humped curve is at first sight unusual, but it has been observed before in some experiments with Michel pads.[3]

The hump can be explained quite simply if two assumptions are made. These are, first, that the initial contact is made by a few outstanding peaks or grinding " fuzz " which stands above the general level of the surface roughness. The main area of the surface will therefore not come into contact till the film thickness is very much smaller. The second assumption is that the initial frictional drag (that is the main part of the

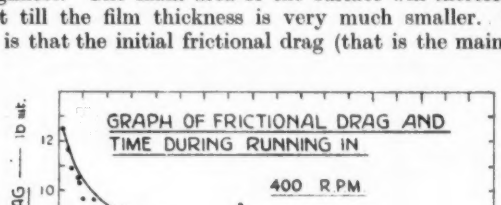

FIG. 3.

frictional drag on initial metal-to-metal contact) is a function of, or is proportional to, the *number* of peaks in contact. This implies that the friction is caused by the peaks welding on to the opposing surface and being torn out bodily. Experimental evidence that this process does occur in a rubbing system has been obtained by Bowden and Moore.[4]

With these two assumptions the course of events can be explained as follows : when the film thickness decreases to a certain value, the outstanding peaks come in contact with the opposing surface. They then weld together, and the frictional drag increases. Until the main surface area comes into contact (at a considerably smaller film thickness) the frictional drag does not go up very much as the film thickness is decreased, as the number of peaks coming into contact (and hence the frictional drag) is not greatly increased. The coefficient of friction, which *rose* sharply on initial contact, therefore *falls* again, as the load is being increased all the time. When all the roughnesses come into contact, the drag and the coefficient of friction increase rapidly to seizure.

It is not possible to comment yet on the step-wise friction–time curve shown in Fig. 3. The Russian work mentioned above shows that a similar phenomenon has been noted with the rate of wear, but the conditions under which the work was done have not been discovered.

Further experiments will be done to try and gain more insight into the mechanism of it.

Further Work.

The machine can be modified further to enable the electrical resistance of the oil film to be measured. For this to be done the block must be insulated from the rest of the machine, which is a simple change. This will enable one to see how far the system is running under fluid conditions.

Further the thermo-electric voltage can be measured in the mixed friction region, which will give a more accurate measure of the true temperature, and hence the viscosity of the oil. Wear of the bronze block can be measured very simply as the block is wider than the cup; the untouched "land" can thus be used as a reference surface.

Acknowledgments.

The author wishes to thank Professor J. F. Baker and members of the staff of the Engineering Laboratory, Cambridge University, for their assistance and also the members of the Part II (B) class of the Mechanical Science Tripos for their work.

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THERMAL DECOMPOSITION OF LEAD MERCAPTIDES.

By Geo. E. Mapstone,* (Member).

Summary.

The thermal decomposition of lead mercaptides in gasoline solution is a first-order reaction with respect to the mercaptan content. The effect of temperature on the reaction-rate constant is given by $\log k = 10{\cdot}63 + 4254/T$. The mechanism of the decomposition is discussed.

In the doctor treatment of gasoline, mercaptans are converted to lead mercaptides by treatment with a solution of litharge in caustic soda.

$$2RSH + Na_2PbO_2 \longrightarrow Pb(SR)_2 + 2NaOH$$

In the normal course of treatment the mercaptides are then oxidized with sulphur, the net effect being the replacement of the original mercaptans by the less objectionable organic disulphides.

$$Pb(SR)_2 + S \longrightarrow PbS + RSSR$$

The plumbite solution is then regenerated by blowing with air.

During an investigation of the properties of solutions of lead mercaptides in gasoline, it was observed that, even in the absence of elemental sulphur, the mercaptides decomposed slowly on standing, and more rapidly on exposure to sunlight.[1] Subsequently it was found that, on boiling relatively strong solutions of lead mercaptides, a black precipitate of lead sulphide was thrown down. Consequently, it appears that the lead mercaptides were decomposed thermally to give lead sulphide and organic sulphide, a reaction which has been observed previously.[2, 3, 4, 5]

The reactions involved in the thermal decomposition of lead mercaptides could be expressed as

$$Pb(SR)_2 \longrightarrow PbS + R_2S$$

for the normal mercaptides and

$$2Pb(OH)SR \longrightarrow Pb(OH)_2 + PbS + R_2S$$

for the basic mercaptides which are also present.[2]

The purpose of this investigation was to determine the mechanism of these reactions.

The rate of the decomposition of lead mercaptide with respect to the mercaptan present was determined at various temperatures for four different samples of sour gasoline and for solutions of *n*-butyl mercaptan in kerosine and benzene.

Experimental.

Approximately 1·8 litre of the sour gasoline were stood in a brown-glass Winchester in the constant-temperature bath and allowed to come to bath temperature. 100 ml of sodium-plumbite solution (containing 100 g

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sodium hydroxide and 20 g litharge per litre) were brought to bath temperature and then added to the sour gasoline and shaken well for 1 min. If a yellow solid separated (excess lead mercaptide) the gasoline was filtered and then brought to bath temperature again before withdrawing the first sample for analysis.

Portions of the mercaptide solution were withdrawn at various times, acidified immediately to hydrolyse the mercaptide, and the mercaptan-sulphur content determined by the modified Borgstrom and Reid method.[6, 7] The time of reaction was taken from when the first sample was withdrawn for analysis.

During the progress of the work it was found that several precautions were essential to the success of the experiment.

(*a*) Failure to protect the sample in the bath from strong light gave high results due to photochemical decomposition of the lead mercaptide. A lead-mercaptide solution exposed in a clear bottle in a window, but not in direct sunlight, was sweetened in less than an hour and a half, while it required three days at the same temperature in a brown-glass bottle in a water-bath.

(*b*) If the mercaptan content of the gasoline was too high, excess lead mercaptide over that required to give a saturated solution was precipitated as a yellow solid when the plumbite solution was added. If this precipitate was not removed, part was continually redissolving as the thermal decomposition progressed and gave apparently variable and low decomposition rates.

(*c*) When the sample was withdrawn for analysis it was pipetted directly into a flask containing 5 ml of the sulphuric-acid–iron–alum indicator and shaken well to decompose the mercaptide. This step was also carried out away from direct daylight. These two precautions were necessary to prevent extensive photochemical decomposition of the sample before it could be analysed.

(*d*) The lead sulphide produced by the decomposition remained in suspension in the gasoline as it was extremely finely divided. In the analysis, however, it generally collected in the aqueous phase and, particularly with the higher-mercaptan-content samples, it completely obscured any colour changes. This was simply overcome by the addition of 0·1 to 0·2 g of fuller's earth, which coagulated the black lead sulphide.[8] This analytical procedure is very simple and effective.

The following six samples were used during the work and are subsequently referred to by number.

(1) A low-boiling gasoline fraction boiling to 280° F.
(2) Full-boiling-range gasoline of F.B.P. 380° F.
(3) Similar to No. 2 with a greater proportion of lower boiling material.
(4) Similar to No. 1, but of different origin.
(5) *n*-Butyl-mercaptan solution in kerosine.
(6) *n*-Butyl-mercaptan solution in benzene.

Some typical results are listed in Table I, and the first-order reaction-rate constants for all experiments are listed in Table II and presented graphically in Fig. 1.

TABLE I

Typical Results of Decomposition

Exp. No.	Samples.	Temp, °C.	Time, min.	Mercaptan [1] content.	$\frac{10^5}{t}\log\left(\frac{a}{a-x}\right)$.
6	1	17·2	nil	103·5	—
			1410	44·5	25·8
			2820	25·5	21·6
			3990	14	21·8
					Aver. 23·1
24	6	26·7	nil	20	—
			1320	6	39·6
			1890	4	36·5
					Aver. 38·0
25	6	32·2	nil	19	—
			240	14	55·2
			360	11	66·1
					Aver. 60·6
11	2	37·8	nil	29	—
			120	22	100
			240	17·5	86·2
			270	17	86·0
					Aver. 90·7
19	3	43·3	nil	80	—
			30	67	257
			60	54	284
			90	42	311
					Aver. 284
18	3	48·6	nil	79	—
			20	66	392
			100	34	366
			120	25	415
			140	22	397
			160	15	452
					Aver. 406

[1] Expressed as p.p.m. of mercaptan sulphur by weight. The results are the mean of duplicate analyses.

DISCUSSION.

The analyses were carried out in duplicate and were normally reproducible to 1 p.p.m. of mercaptan sulphur by weight. This accuracy has been usual for work carried out in the laboratories,[7, 8] although the quoted reproducibility of the method is 50 p.p.m. by weight (0·005 per cent) of mercaptan sulphur.[9]

Because of the low solubility of the lead mercaptides, many of the tests were carried out with initial mercaptan-sulphur concentrations of the order of 20 to 30 p.p.m., and in only one case was it greater than 100 p.p.m. Consequently the accuracy of the analyses was within 1 per cent as a maxi-

TABLE II

Reaction Rate Constants.

Exp. No.	Sample No.	Initial p.p.m. mercaptan sulphur.	Temp, °C.	$\frac{10^3}{T°K}$.	$\frac{10^5}{t} \log\left(\frac{a}{a-x}\right)$.
23	5	19	11·0	3·52	4·4
17	3	87	11·1	3·52	23·4
21	5	14	12·8	3·50	9·3
6	1	103·5	17·2	3·45	23·1
24	6	20	26·7	3·33	38·0
20	4	40	27·0	3·33	55·1
25	6	19	32·2	3·28	60·6
11	2	29	37·8	3·22	90·7
13	2	41	38·9	3·21	111
19	3	80	43·4	3·16	284
15	2	38	45·6	3·13	265
18	3	79	48·6	3·10	406
12	2	34	48·9	3·10	335
27	6	14	48·9	3·10	410

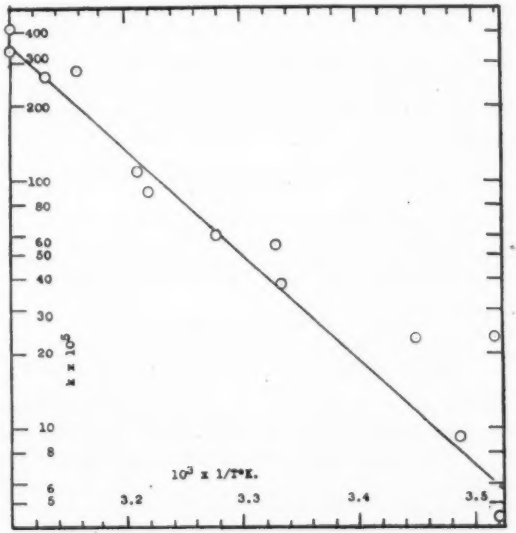

FIG. 1.

CORRELATION BETWEEN REACTION RATE CONSTANT AND TEMPERATURE.

mum, and frequently errors due to this factor could have been greater than 10 per cent of the result at the end of an experiment.

Exposure of the mercaptide solution to light gave anomalous high results due to photochemical decomposition, while failure to remove all precipitated lead mercaptide gave anomalous low results due to re-solution. These two factors were responsible for the discarding of approximately

half the results. Since slight photochemical decomposition was the more difficult to detect, more high than low erroneous decomposition rates would be expected.

Those experiments which were considered to be reasonably accurate were found on closer examination to give first-order reaction-rate constants. Some of the typical results in Table I show the variations obtained, and all final results are listed in Table II. In no case did the results give a second-order reaction constant.

An interesting feature is that the rate of decomposition appears to be independent of the particular mercaptans present or the composition of the gasoline phase. This is shown by the fact that there is no significant difference between the results using six different samples of varying mercaptan and hydrocarbon composition.

A first-order reaction is to be expected for the thermal decomposition of the normal lead mercaptides.

$$Pb(SR)_2 \longrightarrow PbS + R_2S$$

As written, the decomposition of the basic lead mercaptides is a second-order reaction.

$$2Pb(OH)SR \longrightarrow Pb(OH)_2 + PbS + R_2S$$

Since, however, the reaction has been shown to be of the first order and the proportion of the basic mercaptide formed is not negligible, it appears that the decomposition most probably involves the ionization of the mercaptides thus :—

$$Pb(OH)SR \longrightarrow Pb^+(OH) + RS^-$$

and

$$Pb(SR)_2 \longrightarrow Pb^+SR + RS^-$$

followed by the reaction of the mercaptide ion either with the remainder of the molecule or with another molecule of lead mercaptide

$$RS' + RSPb^+ \longrightarrow R_2S + PbS$$

or

$$RS' + RSPbOH \longrightarrow R_2S + PbS + OH^-$$

Because of the effect of photochemical decomposition discussed earlier, the empirical correlation between the reaction-rate constant and the temperature shown in Fig. 1 was taken through the majority of the points but below the median.

This correlation may be written as

$$\log k = 10{\cdot}63 - \frac{4254}{T}$$

where k is the reaction rate constant and T is the absolute temperature.

This gives the energy of activation for the decomposition as 3·66 k.cal per g mol, a value very much lower than that usually obtained for chemical reactions proceeding at measurable rates. The low value obtained for the energy of activation is, however, in agreement with the proposed mechanism of the reaction, if the rate-controlling reaction is the ionization of the lead mercaptide. This appears reasonable as the lead–sulphur bond is un-

doubtedly covalent in the lead mercaptide, but would be expected to ionize fairly readily and therefore require a low energy of activation. Since the hydrocarbon solvent is non-polar the velocity of the ionization reaction would be expected to be slow.[10] Furthermore, the fact that the presence of a range of different mercaptans in the gasoline samples tested did not effect the velocity constant, indicate that the rate-controlling reaction was probably the breaking of the lead–sulphur bond.

Application.

Several processes have been developed in the past few years to remove mercaptans from gasoline rather than to oxidize them to the disulphides in order to reduce the sulphur content of the product. The thermal decomposition of the lead mercaptides may therefore be of commercial application as a sweetening process. For example, decomposition of lead mercaptides is 99 per cent complete in 10 min at 102° C and in 24 hr at 42° C. Mixing with doctor solution and then separating and standing for the required time at the chosen temperature followed by water washing and sand filtration would give a sweet gasoline without the expense and inconvenience of adding sulphur, and with a sulphur reduction of half the initial mercaptan-sulphur content.

Installation of suitable lights in the top of the reaction tank may greatly speed up the decomposition. However, once some lead sulphide has been precipitated, it renders the gasoline opaque and would thus reduce the efficiency of the photochemical decomposition.

Acknowledgments.

The author wishes to acknowledge with thanks the permission granted by the management of National Oil Pty., Ltd., for the publication of this paper, and the assistance of R. J. Dalton in carrying out the work.

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OBITUARY.

A. G. FORBES.

It is with regret that we announce the death recently of A. G. Forbes, a Fellow of the Institute and for the past two years chairman of Standardization Sub-Committee No. 2 on Crude Oil.

In 1908 he started his career in the oil industry by joining the Oakbank Oil Company, Mid-Calder, near Edinburgh, as assistant chemist. In 1913 he went to Burma, where he was employed by the Burmah Oil Co. and in 1918 was appointed chief chemist to the British Burmah Petroleum Co. at Thilwa. In 1918 he left the East and took up a position with the British Controlled Oilfields in Curacao and Maracaibo. He returned to England in 1926 to join the Stanford-le-Hope staff of Cory Brothers & Co. and two years later went to Fawley for the Agwi Petroleum Corporation (now Anglo-American Oil Co.).

His cheerful personality will be missed by all his associates.

G. N.

T. G. MADGWICK.

The death of T. G. Madgwick at the age of seventy-one in Ottawa on December 14, 1948, after a brief illness will be lamented by his many friends and mining associates. He could rightly claim to be one of the pioneer oil geologists who guided early British oil companies in their international developments.

Madgwick received his education at Lewes Grammar School, and Neue Realschule zu Kassel, Germany, before entering the Royal School of Mines in 1896 and leaving with distinction in 1899. During that period his field work included a course in the Westlodge Colliery, Ynysddu, Monmouthshire, and a tour of mines and smelters in Germany. From 1899 to 1902 he was employed as assistant mining engineer to the Ashanti Goldfields Corporation on the Gold Coast, and often related to the writer his amazing underground experiences when the rich gold shoots of the Ashanti mine were being developed. In 1903 he accepted service with the Russian Petroleum & Liquid Fuel Company, and the Baku Russian Petroleum Company, and here he obtained his first oilfield experience as geologist and helper in drilling and production methods. During 1907 and 1908, except for a short period with Messrs Thompson & Hunter undertaking some oil duties, he worked first on the Orsk goldfields in Russia and then with the Urquhart Group of Mining prospects in Siberia and the Urals, and in that capacity was identified with the acquisition of the Kyshtim mining estates, which became the nucleus of the Russo-Asiatic Consolidated. He also reported upon the silver mines of Salair in the Altai Mountains. For a brief period in 1909 he worked under Dr Hayes of the U.S.G.S. in Mexico for the Pearson petroleum interests.

Madgwick rejoined the firm of Thompson & Hunter in 1910, and in the

period prior to the first world war he undertook investigations of oil lands and properties in the United States (Illinois, Ohio, Pennsylvania, West Virginia, Kansas, and Oklahoma), Mexico, Trinidad, Dutch Guiana (Surinam), Argentine, Bolivia, Peru, Poland, Roumania, and Russia, besides assisting in the organization of topographical and geological surveys in other countries. His studies of the Maikop district of Russia did much to elucidate the structure of that field which later became such a prolific producer. As leader of an important expedition to the Eastern Andean foothills of Bolivia, a number of favourable oil structures were located and oil of good quality was obtained in prospecting wells drilled. These early results have been followed by the development of important oilfields in the Chaco. Another interesting oil investigation undertaken was in Bokhara, Central Asia.

Following on the outbreak of war he, in 1915, accompanied A. Beeby Thompson to the Dardanelles on water and supply duties, and until seconded to the Egyptian Government in 1917 he was attached to the Water Division of the Royal Engineers, M.E.F., and performed valuable services in geological studies and supervising drilling and water-service operations in the Dardanelles and in Macedonia.

During 1918 and 1919 he collaborated with other geologists in geological work for the Egyptian Government, during which interesting oil localities in Sinai and on the African side of the Gulf of Suez were mapped under the general direction of Dr Hume, Director of the Geological Survey of Egypt. The reports on the surveys were published under the name of the participants by the Egyptian Government.

On the retirement of Sir John Cadman in 1920, Madgwick accepted the Chair of Petroleum Technology at the University of Birmingham, and spent two years endeavouring to devise an appropriate petroleum course, but he eventually relinquished the post to undertake oilfield investigations in the Hejaz, Egypt, Peru, and the Persian Gulf. It was when reporting upon water prospects in Bahrein that he recognized the oil possibilities of the island and advised an application for oil rights. After adverse conclusions had been reached by various oil interests approached, the concession was acquired by American interests, with results that are common knowledge.

The post of petroleum engineer to the Canadian Department of the Interior was accepted in 1926, and whilst occupying that position he acted as assistant supervisory engineer in the Administration, and was engaged in investigating problems created by the somewhat unusual disclosures in the Turner Valley oilfield. Whilst in the Calgary office he was called upon to correlate and interpret a mass of data derived from drilled wells in Alberta, as well as to study reports of mining prospects in Northern Canada. His immediate chief, Charles G. Ross, was eventually appointed Minister of Lands and Mines of the Province of Alberta. When transferred to Ottawa in 1932 he was attached to the Mines Branch of the Mines and Resources Department, and remained there until his retirement in 1946.

T. G. Magdwick was a keen and conscientious scientist whose geological deductions were always sound. He had the gift of clear expression, and his reports like his remarks were succinct. Hesitation in committing himself to predictions or statements liable to be interpreted as optimistic

was a weakness for which good excuse could be found. Those acquainted with his work were well aware of the value that should be placed on any deductions submitted. The writer found him a loyal and willing collaborator, always ready to undertake missions abroad and give aid whenever it was requested.

He leaves a wife, Hilda Mary, and a son, Commander F. T. C. Madgwick, R.C.N., and a daughter, Dorothy, to whom all friends extend sympathy.

A. B. T.

CORRESPONDENCE.

"*Emulsions of Sea Water in Admiralty Fuel Oil with Special Reference to their Demulsification.*"

To the Editor, *Journal of the Institute of Petroleum.*

SIR,

Our attention has been drawn to the paper in the November issue of the *Journal* on the subject of "Emulsions of Sea Water in Admiralty Fuel Oil with Special Reference to Their Demulsification," by Dr Lawrence and Mr Killner. This paper is, of course, complementary to that read to the Institute of Marine Engineers, a year or so ago, by Admiral Gray and Mr Killner.

The present paper opens with the following bald statement: "Present-day fuel oils emulsify water readily and form mixtures of great stability." The use of the words "readily" and "great" in this assertion is very misleading and the whole statement, in the absence of some indication of the conditions involved, appears likely to give a wrong impression.

In the paper delivered by Gray and Killner there was a tendency to refer to the Admiralty type of fuel oil as though this were representative of all boiler fuels. This misleading impression is accentuated when a statement to the effect that present-day fuels readily form emulsions of great stability is printed in an important petroleum journal.

We have no reason to believe that commercial fuel oils emulsify as readily as Dr Lawrence's paper would indicate: indeed, we have found the greatest difficulty in discovering bulk samples of suitable sludges for use in demulsification experiments of our own.

As the paper which you have published may very probably be quoted by marine technical and other journals, we should like our views upon this matter to be given suitable publicity.

Yours truly,

For THE SHELL PETROLEUM COMPANY LIMITED

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